[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THE DECOMPOSITION OF QUATERNARY AMMONIUM HYDROXIDES. ALKOXYMETHYLDIETHYL-METHYL-AMMONIUM HYDROXIDES

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RECEIVED NOVEMBER 10, 1926 PUBLISHED JULY 5, 1927

The thermal decomposition of quaternary ammonium compounds usually proceeds according to one of three reactions.

$$(R_4N)X \longrightarrow R_3N + RX \qquad (1)$$

$$(R_4N)OH \longrightarrow R_3N + ROH \qquad (2)$$

$$(RCH_2\text{—}CH_2\text{—}NR_3)OH \longrightarrow R_3N + RCH{=}CH_2 + H_2O \qquad (3)$$

The work of earlier investigators has been reviewed by v. Braun[1] who concluded that if the four R groups are not alike, the group which appears as RX (Equation 1) upon decomposition will depend upon the relative reactivities of the groups present. He arranged certain groups in the decreasing order of their reactivities as follows: allyl, benzyl, methyl, ethyl, propyl, *iso*butyl, *iso*-amyl, . . . . . . . . . . .phenyl.

v. Braun also determined the order of reactivity of the various groups for the hydroxides (Equations 2 and 3) and found certain differences from the order given for other negative ions. In the order of decreasing reactivity he found them to be allyl, benzyl, ethyl, propyl, *iso*-amyl, methyl, *iso*butyl, . . . . . . . . phenyl. In another series of experiments he determined the effect of the length of the carbon chain and the effect of certain substitutions upon the tendency of the group to split off as compared to the methyl group, and concluded that the symmetry of the ethylene formed, together with certain factors regarding conjugation of the unsaturated groups, determined the velocity of the rupture.

## Discussion of Results

The present paper deals with the decomposition of quaternary bases of the type $[ROCH_2\text{—}NR_3]OH$. Robinson and Robinson[2] distilled a solution of butoxymethyldiethyl-methylammonium hydroxide and found only methyldiethylamine among the basic decomposition products. This result has been confirmed in the case of the ethoxy derivative and would appear to indicate a higher degree of reactivity for the $(RO\text{—}CH_2\text{—})$ group than for the ethyl group.

The fact that the tertiary bases hydrolyze readily in aqueous acid according to the equation $R'O\text{—}CH_2\text{—}NR_2 + H_2O + H^+ \longrightarrow R'OH + CH_2O + (R_2NH_2)^+$ suggests that this abnormal reactivity of the alkoxymethyl group is to be associated with hydrolysis of the ether linkage. However, the quaternary salts decompose very slowly or not at all in

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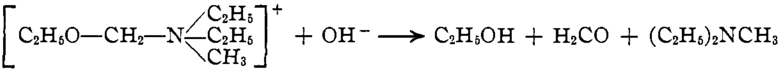
[1] v. Braun, *Ann.*, **382**, 1 (1911).

[2] Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

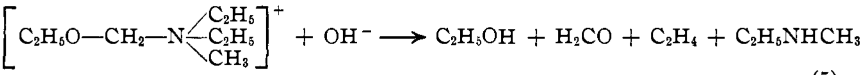
aqueous acid or dilute alkaline solutions at 100° and it will be shown that the same factors which cause the rupture from nitrogen of the alkoxymethyl group also effect the rupture of the other alkyl groups. It will also be shown that the proportion of alkoxymethyl to methyl or ethyl groups which split off is a function of the temperature.

The decomposition of ethoxymethyldiethyl-methylammonium hydroxide has been studied under three conditions. First, a solution of the base was evaporated slowly (during ten days) in a vacuum desiccator at room temperature; second, a similar solution was evaporated more rapidly (two days) at room temperature in a vacuum; third, a solution of the hydroxide was concentrated by distillation at atmospheric pressure.[3]

The results of the three experiments can be expressed by two equations.



$$\left[C_2H_5O{-}CH_2{-}N\begin{matrix}C_2H_5\\ C_2H_5\\ CH_3\end{matrix}\right]^+ + OH^- \longrightarrow C_2H_5OH + H_2CO + (C_2H_5)_2NCH_3 \quad (4)$$



$$\left[C_2H_5O{-}CH_2{-}N\begin{matrix}C_2H_5\\ C_2H_5\\ CH_3\end{matrix}\right]^+ + OH^- \longrightarrow C_2H_5OH + H_2CO + C_2H_4 + C_2H_5NHCH_3 \quad (5)$$

The only difference between the first and second experiment was the time required for the decomposition. The products found were practically identical in the two cases, and indicated that 18.5% of the reaction took place according to Equation 4, and 81.5% according to Equation 5. The results of the third experiment, at the higher temperature, indicated that at least 90% of the reaction took place according to Equation 4.

The rate of rupture of the alkoxymethyl and of the ethyl groups is thus the same function of the rate of pumping or rate of evaporation of water from the solution. As a solution of the base becomes concentrated at room temperature, no decomposition occurs until the sirupy liquid approaches a composition corresponding to between a tetra- and pentahydrate. The reaction begins suddenly, proceeds at a constant rate, depending upon the surface exposed and the pressure, and stops as suddenly as it started.[4]

The relative activities of the three groups at room temperature are as follows: $C_2H_5 > C_2H_5OCH_2 > CH_3$. Above 100° the relative reactivities are $C_2H_5OCH_2 > C_2H_5 > CH_3$. It is apparent that the order of reactivity may be changed by a change in the temperature at which

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[3] This was the method used by nearly all of the previous investigators.

[4] In one instance a sample contained in a weighing bottle was slowly evaporated for a week. It started to give off gas (ethylene and amines) within a given half-hour, and while held at constant pressure gave off gas bubbles only from the surface at practically constant rate, as measured by the time necessary to build up to a given pressure or as measured in other instances by a sulfuric acid bubbler in the line. The apparent equivalent weight remained constant throughout the decomposition.

the decomposition is carried out, and that the reactivity of the ethoxymethyl group is closer to that of ethyl than to that of methyl.

The decomposition of *iso*butoxymethyl-trimethylammonium hydroxide, $C_4H_9OCH_2—N(CH_3)_3OH$, under the same conditions as in the second experiment described above, yielded trimethylamine as the only volatile base.

The question of whether a tetrahydrate, a lower hydrate, or anhydrous molecule is the species which decomposes cannot be answered. If the evaporation and decomposition at room temperature proceed at a higher total pressure, and therefore more slowly, bubbles form throughout the mass instead of solely at the surface, suggesting that whatever is formed by evaporation at the surface has time to diffuse to some depth (about 1 to 2 cm.) before decomposing, or that water from the body of the solution has time to diffuse to the surface so that the composition is constant throughout the mass. In such a case the equivalent weight more nearly corresponds to that of a tetrahydrate than in the case of a more rapid evaporation where the surface layer only is kept at a composition which promotes decomposition. At a very low pressure (0.001 mm.) and temperature (—20°), evaporation proceeds slowly without apparent bubbling, but as soon as the temperature is raised, even at atmospheric pressure, evolution of gas begins. These facts seem to indicate that hydrate formation stabilizes the quaternary ion in the presence of hydroxide ion.[5]

Another important fact, namely, that hydroxide and carbonate ions cause the formation of ethylene as well as of alcohol, must be accounted for and possibly connected with the relative rates of rupture from the nitrogen of the various groups under consideration. It seems probable that the instability of an "onium" compound lies in the tendency of the charge on the central atom to become neutralized at the expense of a shared electron with the consequent loss of a positive ion.

The ease with which a quaternary ammonium compound will decompose will then depend upon two factors; first, the tendency of the nitrogen atom to lose the positive charge, with the loss of one of the groups as a positive ion, and second, the reluctance of the bound groups to split off as the positive ion. This reluctance is less if the presence of certain groups (ethylene bonds, oxygen atoms) may serve to distribute the positive charge along the group in question, and hence reduce the intensity of the positive charge upon the nitrogen atom. Another means of reducing the charge upon the nitrogen or upon the carbon atoms is the dissociation of a hydrogen atom. A reactive hydrogen upon an atom sufficiently

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[5] Very few quaternary bases decompose rapidly in dilute aqueous solution, even at 100°. Of these may be mentioned those of the type $[R_3NOR']OH$, which in dilute aqueous solution at room temperature slowly decompose to give the tertiary amine $R_3N$, water and the aldehyde or ketone corresponding to the radical R′. The substance $[C_6H_5CH_2CH_2—N(CH_3)_3]OH$ also decomposes in dilute solution, upon heating.

near the nitrogen, through its oscillation if not actual ionization, could in effect reduce the intensity of the charge upon the nitrogen and carbon, and facilitate the rupture reaction. The role of the hydroxide ion then becomes clear. It acts either as an agent to aid in the removal of hydrogen ion from the molecule, or to replace the tertiary amine nitrogen in the quaternary ion. The former reaction explains its specific action in hastening decompositions which do not take place in acidic solution and in causing the formation of ethylenes.[6]

The decomposition does not involve ions, in the sense that there exists at any time appreciable amounts of either alkyl or hydrogen ions in the solution, or that either of these ions is formed as a *reversible* first step in the decomposition. We may rather look upon the decomposition, when an ethylene is formed, as preceded by the *simultaneous* loosening of the carbon-nitrogen and carbon-hydrogen bonds. This is followed by the simultaneous loss of hydrogen ion, rupture of the carbon-nitrogen bond, and rearrangement of the carbon residue to a stable ethylene. The relative rates of the decompositions will then depend upon the capacities of the various groups to reduce the intensity of the positive charge through minor rearrangements of electrons and protons within the group. The loss of hydrogen ion to form water, in the presence of hydroxyl ion, will cause a more rapid rupture of a given group. If this last reaction could be excluded, it is probable that the relative rates of decomposition of different groups in salts and in quaternary bases would be identical.

The stabilizing effect of water upon the quaternary ion may be attributed to the same sort of factor that promotes the decomposition. The hydration of the ion serves to distribute the positive charge over what is essentially a larger molecule, thereby lowering the intensity of the charge upon the nitrogen. There is, therefore, less tendency for the carbons or hydrogens to assume a positive charge.

## Experimental Part

### Decomposition of Ethoxymethyldiethyl-methylammonium Hydroxide at Room Temperature

**Expt. 1. Qualitative Decomposition.**—A solution of ethoxymethyldiethyl-methylammonium hydroxide was prepared from 20.15 g. (0.074 equivalent) of the iodide and a slight excess of the calculated quantity of silver oxide. It was evaporated at room temperature in a vacuum desiccator over calcium chloride to a volume of about 25 cc., then transferred to a tared weighing bottle and the evaporation continued in a vacuum over phosphorus pentoxide. The solution became viscous and had no odor of amines. When the weight of the residue reached 15.80 g., a froth was observed on the surface, and amine and formaldehyde odors became noticeable. A sample taken at this point, when titrated with standard acid, using phenolphthalein as indicator, showed the

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[6] See Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 135.

equivalent weight to be 248, and the 15.80 g. to contain 0.0636 equivalent of base. The equivalent weight calculated for the tetrahydrate of the base is 235.

The decomposition was continued in a vacuum, the pressure rising at a constant rate from 2 mm. to about 25 mm. in two days. The cessation of the decomposition was abrupt at the end of ten days, leaving a liquid residue. The decomposition products were isolated as follows. Samples of gas aspirated from the desiccator were shown to be a mixture of ethylene and air by the usual methods of absorption and combustion. Most of the amines were contained in the acid drying agent and were recovered by the addition of alkali and by distillation into hydrochloric acid. The pure, dry hydrochloride weighed 5.14 g.

*Anal.* (Volhard). Calcd. for $C_3H_9NHCl$:Cl, 37.15; for $C_5H_{13}NHCl$, 28.71. Found: 35.25.

The analysis corresponds to 18.5 mole % of methyldiethylamine hydrochloride and 81.5 mole % of methylethylamine hydrochloride, shown also as follows. A 4.34 g. sample of the mixed hydrochlorides (containing 0.00431 equivalent of chlorine) was separated by the method of Hinsberg[7] into the tertiary amine and the benzene sulfonamide of the secondary amine. The yield of tertiary amine was 0.000915 equivalent, or 21% of the total amine in the mixed salts. The platinum double salt decomposed sharply at 230°.

*Anal.* Calcd for $(C_5H_{13}NH)_2PtCl_6$: Pt, 33.37. Found: 33.33.

The yield of dry, liquid methylethyl benzenesulfonamide was 5.76 g.

*Anal.* (Kjeldahl). Calcd. for $C_9H_{13}NSO_2$: N, 7.04. Found: 6.96.

Upon hydrolysis, the amide yielded 2.08 g. of an amine hydrochloride; m. p., 126–129.5°.

*Anal.* (Volhard). Calcd. for $C_3H_9NHCl$: Cl, 37.15. Found: 36.90.

The chloroplatinate decomposed at 208–208.5°.

*Anal.* Calcd. for $(C_3H_9NH)_2PtCl_6$: Pt, 36.96. Found: 36.96.

The amines are thus methyldiethylamine and methylethylamine.[8] The proportions of the two given by the chlorine analysis of the mixed salts are probably accurate to about 1%.

The residue from the decomposition was shown to contain salts of the undecomposed base by preparation and analysis of the chloroplatinate. When recrystallized from 50% alcohol the chloroplatinate decomposed at 223.5°.

*Anal.* Calcd. for $(C_8H_{20}ON)_2PtCl_6$: Pt, 27.87. Found: 28.00.

The salts were probably the bicarbonate and formate.

**Expt. 2. Quantitative Decomposition.**—A solution containing 0.0371 equivalent of ethoxymethyldiethyl-methylammonium hydroxide was prepared and concentrated as above. Its equivalent weight was 267 when the decomposition began. As soon as decomposition became evident, the weighing bottle and contents were sealed into a 100cc. tube (Fig. 1), which was sealed to a system consisting of a liquid-air trap (3 cm. × 35 cm.) connected, through a tube containing phosphorus pentoxide, to a hand-operated Töpler pump. The line was pumped out by means of the Töpler pump to 2 mm., at which pressure the liquid in the weighing bottle started to boil. This boiling soon ceased. The system was evacuated to 0.5 mm. At this pressure vigorous decomposition took place and continued for 52 hours.

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[7] Hinsberg, *Ber.*, **38**, 906 (1905).

[8] The chloroplatinates decompose, respectively, at 231° (Ref. 2) and 207–208° [Beilstein, vol. 1, p. 1125]. Hinsberg [*Ann.*, **265**, 180 (1891)] describes methylethylbenzene sulfonamide as a liquid.

After 52 hours, the decomposition stopped as suddenly as it had started, very little material remaining. The liquid air around the trap was replaced by a mixture of solid carbon dioxide and ether. This allowed the ethylene to boil out of the trap and the pressure in the line rose to about $^2/_3$ atm. The system stood overnight in this condition in order to allow time for the formaldehyde to polymerize. The outlet from the pump was then connected to an aspirator (Fig. 2) filled completely with mercury. The ethylene was pumped out of the line into the aspirator until the residual pressure was 11 mm., the displaced mercury being collected in a weighed receiver.[9] The pressure in the aspirator was finally adjusted to atmospheric pressure by leveling the mercury surfaces in the bulb and reservoir of the pump at the three-way stopcock. During the process the adjustable tip forming the outlet of the aspirator was kept below the mercury surface in the receiver, the latter being kept below the mercury level in the bottle. The mercury in the receiver was then weighed.

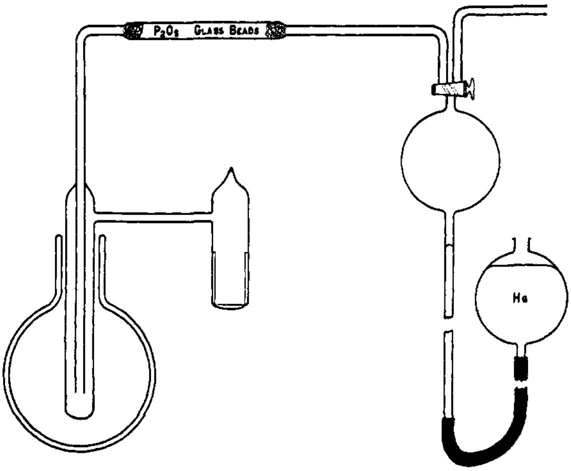

Fig. 1.

The 8091 g. of mercury (596 cc.) displaced by ethylene at 19.1° and 757.1 mm. pressure corresponds to 0.0247 mole of ethylene.

Analysis of the gas showed the absence of amines and the presence of only traces of formaldehyde. A sample was completely absorbed in bromine water. The ethylene remaining in the system was estimated from the volume and residual pressure and the probable amount dissolved in the liquid mixture of amine, alcohol, formaldehyde, etc., at —77°, to be about 0.0012 mole. The total ethylene formed was thus 0.0259 mole and corresponded to the amount of methylethylamine formed (0.0263 mole) within experimental error.

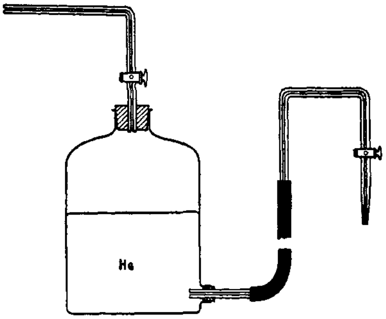

Fig. 2.

After removal of the ethylene, dry air was let into the line and an excess of acid added to the trap, while still in the carbon dioxide-ether mixture. The solution of

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[9] Pumping was not continued further for fear of pumping over formaldehyde. A correction for the remaining ethylene is made later.

amine hydrochlorides was transferred to a large flask and steam-distilled from acid solution to separate the formaldehyde and amines. The solution was then made alkaline and the amines were distilled into a known volume of standard hydrochloric acid which was then back-titrated. The phosphorus pentoxide from the tube was dissolved in water and treated in a similar manner. There was found in the trap 0.03235 equivalent of volatile base and a negligible quantity in the phosphorus pentoxide.

The amines were distilled from an alkaline solution of the titration mixture into an excess of hydrochloric acid, and the water was evaporated, yielding 3.238 g. of mixed hydrochlorides.

*Anal.* (Volhard). Found: Cl, 35.25.

This analysis corresponds to 18.5 mole % of diethylmethylamine, and 81.5 mole % of methylethylamine. A weight of salt corresponding to 0.01207 mole of the hydrochloride was treated with benzene sulfonyl chloride to separate the secondary and tertiary amines as described above. Tertiary amine corresponding to 0.00181 mole was obtained. Assuming this to be diethylmethylamine, as in the previous experiment, this corresponds to 15.0 mole % of the decomposition. The value calculated from the chlorine analysis is to be taken as the more accurate, the estimated accuracy being about 1%.

**Identification of Residue.**—The residue in the weighing bottle weighed 0.8996 g. This was dissolved in water, yielding a solution neutral to phenolphthalein. On boiling, it became alkaline to phenolphthalein. Small quantities of 0.1 *N* sulfuric acid were added and the solution boiled after each addition, until the pink color appeared. Finally, the pink color no longer returned, showing all of the carbon dioxide to have been expelled. The excess of acid was then back-titrated; 0.00101 equivalent of 0.1 *N* sulfuric acid was used.

An excess of sulfuric acid was added and the mixture was steam-distilled, keeping the volume very low, until no more acid came over. The distillate was titrated with 0.1 *N* sodium hydroxide; 31.38 cc. was required. The formic acid was identified by reduction of mercuric chloride; found, 0.00101 equivalent of bicarbonate and 0.00314 of formate; total, 0.0042 equiv. of acid. The nitrogen in the residue from which the formic acid had been distilled was determined by the Kjeldahl method; found, 0.0044 equivalent of nitrogen, which agrees with the quantity of acid found within experimental error.

**Expt. 3. High-Temperature Decomposition of Ethoxymethyldiethyl-methylammonium Hydroxide.**—0.0455 equivalent of ethoxymethyldiethyl-methylammonium hydroxide in a solution of about one equivalent per 1000 g. was taken for the decomposition. The material was contained in a 500cc. Kjeldahl flask with glass beads to prevent foaming. The Kjeldahl flask was fitted with a spray trap and condenser, the latter dipping below an excess of 0.1 *N* hydrochloric acid. The flask was heated to 135° by means of a glycerol bath. At this temperature boiling took place. Almost as soon as distillation commenced, decomposition set in, as indicated by a piece of moist red litmus in the condenser turning to blue, and by the odor of formaldehyde in the receiver. The main part of the decomposition was carried out at 140–150°. When three-fourths of the liquid in the flask had disappeared, the decomposition became much more rapid. These observations seem to indicate only a slight decomposition through hydrolysis in the first stage and that the main decomposition took place after the liquid reached a low water content, just as in the low-temperature decomposition.

After the apparatus had reached temperature equilibrium, only two or three bubbles of gas escaped, showing that no permanent gas was formed.

When all of the material had decomposed, water was run into the flask and the amines were swept out by steam. Back-titration of the distillate showed the formation of 0.03659 equivalent of volatile base.[10] The distillate, after being acidified and steam-distilled, was made alkaline, and the volatile amines were collected in an excess of hydrochloric acid. The solution, after evaporation, yielded 4.61 g. of hydrochloride. Before analysis, the hydrochloride was evaporated with absolute alcohol to remove hydrochloric acid.

*Anal.* (Volhard). Calcd. for $C_5H_{13}NHCl$: Cl, 28.7. Found: 29.4.

This shows that decomposition took place to yield at least 90% of methyldiethylamine.

**Expt. 4. Dehydration of Ethoxymethyldiethyl-methylammonium Hydroxide at —15°.**—A quantity of ethoxymethyldiethyl-methylammonium hydroxide solution, prepared as above (equivalent weight, 267, at the decomposition concentration), was placed in a container cooled to —15° and a vacuum below $10^{-3}$ mm. maintained. After three days, no crystals having appeared, the flask was allowed to come to room temperature, when decomposition took place for a considerable time without pumping. A crystalline hydrate could not be obtained.

**Preparation of *iso*Butoxymethyl-trimethylammonium Iodide and Hydroxide.**—Dimethylaminomethyl*iso*butyl ether was prepared as described by Robinson and Robinson;[2] b. p., 127–128.5°; equivalent wt., 132 (calcd., 131). This compound in 50% ether solution reacts explosively with methyl iodide, at room temperature. A 20% solution of the base in anhydrous ether was cooled in ice, and a 10% excess of methyl iodide in 40% anhydrous ether solution was added, taking care to keep out moist air. A white precipitate formed. When all of the methyl iodide had been added, the solution was removed from the ice and allowed to stand at room temperature for three days. The gelatinous mixture was diluted with dry ether and filtered. The salt was washed with ether and dried; m. p., 110–114°. (In one sample, melting started at 99° and then, almost immediately, the small amount of liquid resolidified. After further drying of the sample, the same phenomenon was noted.) The substance was crystallized from hot butyl alcohol (1 cc. per g.). The recrystallized product (m. p., 103–110°), after several crystallizations, had the same melting point. Other alcohols, tried as solvents, gave no better results. The compound is very soluble in water and alcohols.

*Anal.* (Volhard). (Uncrystallized material.) Subs., 0.3290, 0.2774: 12.56, 10.56 cc. of 0.0958 *N* $AgNO_3$. Calcd. for $C_8H_{20}ONI$: I, 46.50. Found: 46.4, 46.3. (Crystallized material.) Subs., 0.4600, 0.5106: 17.68, 19.66 cc. of 0.0958 *N* $AgNO_3$. Calcd. for $C_8H_{20}ONI$: I, 46.50. Found: 46.7, 46.7.

0.0448 mole of *iso*butoxymethyl-trimethylammonium iodide in 100 cc. of water was shaken with a slight excess of silver oxide until the solution no longer gave a test for iodide ion. The silver iodide was filtered off and the solution evaporated as described for the other quaternary bases. Only a very faint odor of amines was perceived.

About 0.004 equivalent of the base was neutralized with hydrochloric acid and the solution evaporated at room temperature over phosphorus pentoxide in a vacuum. The residue was taken up in absolute alcohol and the calculated quantity of chloroplatinic acid in alcohol was added. The platinum double salt was filtered off and washed with alcohol and ether; decomp. at 229.5–230° (heating started at 20°).

*Anal.* (Ignition). Subs., 0.2776: Pt, 0.0780. Calcd. for $C_{16}H_{40}O_2N_2PtCl_6$: Pt, 27.87. Found: 28.13.

After recrystallizing, a constant decomposition point 231–233° was obtained under

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[10] Complete decomposition was probably prevented, as in the room-temperature decomposition, by the formation of formic acid from the formaldehyde, according to the equation $2H_2CO \longrightarrow HCO_2H + CH_3OH$.

the same conditions. Since the iodide is hard to purify, the decomposition point of the platinum salt may be used to characterize the base.

*Anal.* (Ignition). Subs., 0.1754: Pt, 0.0490. Calcd.: Pt, 27.87. Found: 27.93.

**Expt. 5. Decomposition of *iso*Butoxymethyl-trimethylammonium Hydroxide at Room Temperature.**—The remainder of the solution of the base, after evaporation over phosphorus pentoxide until decomposition took place, weighed 7.51 g. and had an equivalent weight of 231; 0.0325 equivalent of base was thus present. (Calcd. for the tetrahydrate, equiv. wt., 235.) The material in a weighing bottle was sealed up in the line already described (Fig. 1), the trap being surrounded by liquid air, and the line evacuated to 1.5 mm. Further evacuation was not possible because, if the decomposition became too vigorous, serious frothing took place. The decomposition continued for seven weeks.

When the decomposition was complete, the liquid air was replaced by a solid carbon dioxide and ether mixture. There was no increase in pressure in the line, showing that no ethylene was formed.

Air was let into the line and the amines were isolated as the pure hydrochlorides, as before; 0.0028 equivalent of base was found in the phosphorus pentoxide and 0.0204 in the trap; total, 0.0232 equivalent. (The rest of the base could be accounted for in the residue.)

*Anal.* (Volhard). Calcd. for $C_3H_9NHCl$: Cl, 37.15. Found: 37.10, 37.11.

A platinum double salt prepared from this hydrochloride was recrystallized from hot 67% alcohol. Its decomposition point, starting with the bath at 236°, was 240–241°.[11]

*Anal.* (Ignition). Subs., 0.2152: Pt, 0.0794. Calcd. for $(C_3H_9NH)_2PtCl_6$: Pt, 36.96. Found: 36.90.

The decomposition thus yields trimethylamine as the only amine.

**Expt. 6. Decomposition of Dimethyldiethylammonium Hydroxide at Room Temperature. Decomposition of Normal Carbonate.**—Diethyldimethylammonium hydroxide was decomposed by evaporation of a solution in a vacuum desiccator at room temperature. Ethylene, dimethylethylamine and water were the only products formed.

An attempt was made to obtain a crystalline normal carbonate by the evaporation of an aqueous solution of diethyldimethylammonium carbonate at room temperature. Decomposition took place in the concentrated solution, and when an anhydrous solid eventually formed it proved to be the corresponding bicarbonate. This in turn, upon heating, did not give the normal carbonate, but only ethylene, pure ethyldimethylamine, carbon dioxide and water.[12]

**Expt. 7. The Conductivity of Fused Ethoxymethyldiethyl-methylammonium Iodide.**—Anticipating a high specific conductivity of the fused material, the cell shown in Fig. 3 was designed and used for the measurements. The distance between the electrodes was approximately 20 cm. and the cross-sectional area 0.1 sq. cm. The bulbs facilitated the filling of the cell, each being fitted with a calcium chloride tube to protect the material from moisture.

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[11] Knorr [*Ber.*, **22**, 184 (1889)] gives the decomposition point of trimethylamine chloroplatinate as 240–245°.

[12] The authors are indebted to Mr. R. D. Fowler for this result.

The conductivities were measured by comparison with corresponding resistances of a 9999ohm resistance box, using a Leeds and Northrup bridge for the comparison. The cell constant was determined by filling the cell with 1 *N* potassium chloride solution and determining the conductivity at 25°.

About 10 g. of recrystallized ethoxymethyldiethyl-methylammonium iodide (m. p., 84°) was placed in one of the bulbs and the cell immersed in an oil thermostat at 110°. When the material had melted it was drawn from one bulb to the other until the portion of the cell between the electrodes was entirely full.

After the material had been in the thermostat for half an hour, the conductivity was measured, and then again after one hour. No change was observed. The minima were poor and could not be improved by capacity adjustments. A lower conductivity than was expected prevented readings being taken in the middle of the bridge. These two factors introduce an uncertainty of about 5% in the measurements.

The conductivity was determined periodically over an interval of 12 hours, and found to remain almost constant. The temperature of the thermostat was then raised by steps to 140°, the conductivity being determined at intermediate temperatures and at 140°, in order to determine the effect of viscosity. On cooling to 110°, the conductivity had only changed slightly from its original value. A test showed that the material had almost completely decomposed.

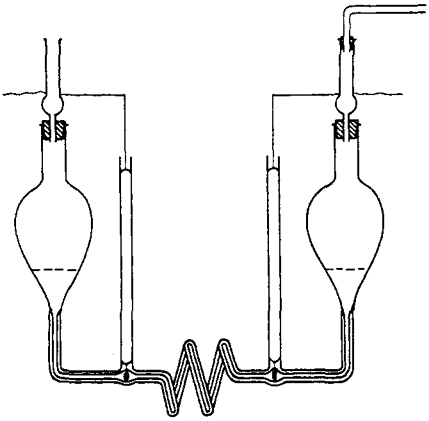

Fig. 3.

An experiment showed, however, that no appreciable decomposition took place on keeping the original material at 110° for one hour. Further,

Table I

Conductivity of the Fused Salt[a]

| No. | Time in thermostat, hrs. | Temp., °C. | Resistance of cell, ohms |
|---|---|---|---|
| 1 | 0.5 | 110 | 19,100 |
| 2 | 1 | 110 | 20,400 |
| 3 | 3 | 110 | 18,400 |
| 4 | 6 | 110 | 18,600 |
| 5 | 18 | 127 | 11,000 |
| 6 | 24 | 135 | 9,000 |
| 7 | 30 | 139 | 7,660 |
| 8 | 60 | 110 | 15,300 |

[a] Cell constant = 245.

the fact that the conductivity of the material changed but slightly on standing at 110° shows that the impurities had little effect on the conductivity. The conductivity at 110°, after half an hour, may thus be assumed not in error by more than 10%. The results are given in Table I. From No. 1 we calculate $\kappa_{110°} = 0.0128$ mho. The density of the fused salt at 110° was found to be 1.3615 g./cc. From these data we calculate $\Lambda_{110°} = 2.56$.

## Summary

*iso*Butoxymethyl-trimethylammonium iodide and hydroxide have been prepared. The electrical conductivity of fused ethoxymethyldiethylmethylammonium iodide has been measured at 110°.

The decompositions of ethoxymethyldiethyl-methylammonium hydroxide and *iso*butoxymethyl-trimethylammonium hydroxide, on dehydration of the solution at room temperature, have been studied and compared with those of simple quaternary ammonium hydroxides under the same conditions. Ethoxymethyldiethyl-methylammonium hydroxide yields 18.5 mole % of diethylmethylamine and 81.5 mole % of ethylmethylamine, with a corresponding amount of ethylene; *iso*butoxymethyl-trimethylammonium hydroxide yields only trimethylamine. Above 100° the former base yields only diethylmethylamine, upon decomposition. A mechanism similar to that in the decomposition of the simple quaternary ammonium hydroxides is involved. The theory of such decompositions is discussed.

Attempts to prepare crystalline hydrates and anhydrous forms of the above hydroxides failed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

# EXTRACTION OF MALTASE FROM YEAST[1]

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RECEIVED NOVEMBER 12, 1926 PUBLISHED JULY 5, 1927

Some years ago we were anxious to prepare an active maltase solution to repeat the experiments of Hill[2] on the action of maltase on a strong glucose solution. As we never succeeded in obtaining a very active maltase solution by the methods given by Hill, we decided to learn more about the extraction of maltase.

We were handicapped by not being able to obtain fresh bottom yeast which is richer in maltase than top yeast. We are, however, very much indebted to the Fleischmann Yeast Company for supplying us at all

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[1] Read before the Organic Section of the American Chemical Society in April, 1924, at Washington, D. C.

[2] Hill, *J. Chem. Soc.*, **73**, 634 (1898).