

carbonate and sufficient oxalate to prevent the precipitation of the aluminum or chromium.

The behavior of these individual elements has been studied and the method is proposed for the qualitative separation of these elements into two groups, to be designated the Zinc Group and the Aluminum Group, respectively.

Experiments have shown that by this method 1 mg. of any element of one group can be separated from as much as 500 mg. of any element of the other group.

As a quantitative method it has been shown that 250 mg. of any element of the zinc group can be precipitated quantitatively from a solution containing 250 mg. of any element of the aluminum group and that less than 1 mg. of any element of the aluminum group will be carried out in the precipitate.

The sulfide precipitates obtained under these conditions are readily coagulated, filtered and washed.

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

## THE MECHANISM OF HYDROLYSIS OF DIALKYLAMINOMETHYL ETHERS

BY T. D. STEWART AND WILLIAM E. BRADLEY

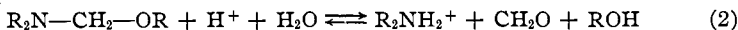
RECEIVED JUNE 14, 1932

PUBLISHED NOVEMBER 5, 1932

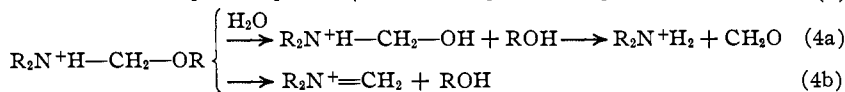
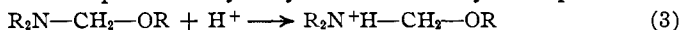
The aminomethyl ethers have been prepared by a modification of the method of McLeod and Robinson.<sup>1</sup>



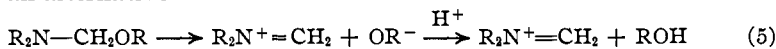
They are very rapidly hydrolyzed in dilute aqueous acid at room temperature, so that merely dissolving the ether in one equivalent or more of acid usually produces the reaction



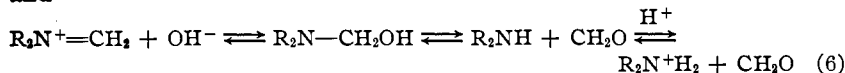
Possible successive steps in the hydrolysis reaction may be represented as



or as an alternative



and

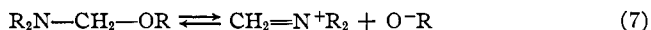


<sup>1</sup> McLeod and Robinson, *J. Chem. Soc.*, 119, 1470 (1921).

There is no doubt that the separation of the alkoxy group precedes rupture of the carbon-nitrogen attachment. It is less certain that ionization of alkoxyate ion is the primary step as represented in Equation (5); an argument in favor of this view will be presented.

A distinction is drawn between the ions,  $R_2N^+=CH_2$  and  $R_2N^+H-CH_2-OH$ , although it is certain that the former is highly hydrated in solution. The latter ion is probably the cation of a very weak base. To the extent that it exists, it is presumed to be stable; the path for its dissociation into aldehyde and amine salt or into the iminium ion lies through the pseudo base, as represented in Equation (6). The iminium ion is usually not isolated in the case of these simple derivatives, either as the salt or as the base. It is proposed to show that it is an intermediate in the separation of the nitrogen and carbon atoms. The reaction thus takes the familiar form usually assigned to the pseudo bases of the pyridinium type.<sup>2</sup>

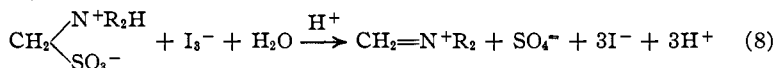
Robinson and Robinson<sup>3</sup> considered, and discarded the view that these amino ethers are a mixture of definite isomers



They preferred to represent the high reactivity to hydrolysis and to the Grignard reagent by the formula  $CH_2 \begin{matrix} \nearrow N^+R_2 \\ \searrow O^-R \end{matrix}$ . The nearest approach to an actual isolation of an iminium salt has been a platinum double salt, having a composition corresponding to the formula,  $(CH_2Cl-NR_2H)_2PtCl_6$ ,<sup>4</sup> which could be simply the chloroamine chloroplatinate.

Stewart and Aston<sup>5</sup> measured the relative base strengths of the amino ethers in absolute alcohol, and considered that they were measuring the equilibrium of Equation (3). They prepared a hydrochloride in dry ether, which contained alcohol, presumably the simple hydrogen chloride addition product. In alcohol they observed nothing to indicate a dissociation of the alkoxy group.

**Preparation and Properties of N-Diethylmethylene Iminium Chloride.**—Our first observance of the existence of the ion  $CH_2=N^+R_2$  came in a study of diethylaminomethyl sulfonic acid, in its reaction with iodine solution.



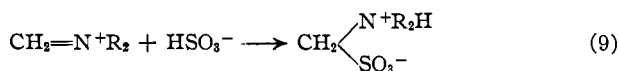
The reaction is relatively slow, being half over in from eight to ten minutes. The resulting solution uses up bisulfite ion instantaneously, so that formaldehyde is not a reaction product, since it reacts slowly with bisulfite at the hydrogen-ion concentrations used.

<sup>2</sup> Aston, *THIS JOURNAL*, **52**, 5254 (1930).

<sup>3</sup> Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

<sup>4</sup> Houben and Arnold, *Ber.*, **41**, 1575 (1908).

<sup>5</sup> Stewart and Aston, unpublished data.



The presence of diethylammonium salts does not affect formaldehyde in this respect. Moreover, the sodium bisulfite addition product of formaldehyde in acid solution does not react at all with iodine, whereas the aminosulfonic acid reacts slowly at a rate independent of the iodine concentration. The cycle of reactions—slow iodine titration, sulfite addition, slow iodine titration—could be repeated at will, and quantitatively within one per cent. It thus appears that the product of the reaction with iodine is not formaldehyde and the secondary amine as such, but a compound of the two.

Excess of the iodine solution produced an oily precipitate which was collected in a separate experiment and washed with potassium iodide solution until the ratio of titratable iodine to nitrogen in the washings approached a constant value. The composition of the oil agrees with the formula,  $\text{CH}_2\text{I}-\text{NR}_2\text{I}_4$ , and suggests an association of iodide ion, or triiodide ion, with the iminium ion, and an additional association of iodine as amine periodide. This is the only evidence we now have of association of halogen ions with these iminium ions.<sup>6</sup>

The reactions of the iminium ion with bisulfite ion and with periodide ion furnish tools by which its presence in solution may be detected. When an  $\alpha$ -aminomethyl ether is added drop by drop with vigorous stirring to one normal acid, the usual production of formaldehyde and amine salt is not observed. Instead, the solution has the same characteristics as the solution produced by adding iodine to the  $\alpha$ -aminosulfonic acid. It reacts with bisulfite instantly to form the  $\alpha$ -aminosulfonic acid, which in turn reacts with iodine at its characteristic rate. It is not the amino ether as such that reacts with the bisulfite ion, as the alcohol formed according to Equation (5) may be removed by vacuum distillation without affecting the reaction of the solution toward bisulfite.

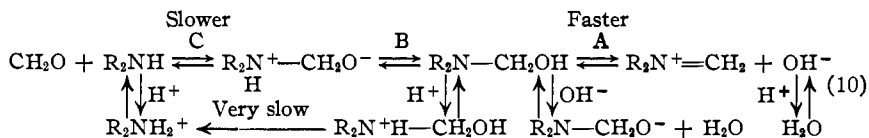
The validity of Equation (5) was further established by the actual isolation, in one instance, of a salt of the composition  $\text{CH}_2=\text{N}(\text{C}_2\text{H}_5)_2\text{-Cl}\cdot 6\text{H}_2\text{O}$ . *N*-Diethylaminomethyl isobutyl ether was rapidly neutralized

<sup>6</sup> The  $\alpha$ -halogenoamines are usually unstable salts, of which the imido ester salts are examples, and are therefore to be considered as iminium salts. Pararosaniline color (pseudo) base in acid similarly forms a strong salt. If, however, the onium property of the nitrogen atom is completely neutralized by quaternary amine formation, a halogen in the alpha position is remarkably stabilized. For instance, iodomethyltrimethylammonium ion is difficult to hydrolyze, as are the alkoxymethyltrialkylammonium ions. The mobility of the halogen in the hypothetical halogenoamines is therefore dependent upon the capacity of the nitrogen to share its electron with the adjacent carbon, and the above association of iodide ion and iodine is evidence of both the weak salt-forming tendencies of iodide ion and the neutralization of the amine by periodide formation.

to the methyl orange end-point with 1 *N* hydrochloric acid, and the solution evaporated *in vacuo* over calcium chloride. The crystalline salt was kept for several weeks without decomposition except to form a tetrahydrate. Attempts to repeat the preparation failed, and yielded only formaldehyde and diethylammonium chloride. The one success was probably due to a fortuitous use of the right excess of acid, and illustrates the sensitiveness of these molecular systems.

**Reactions with Alkali.**—Equation (6) represents the reaction of hydroxide ion with the iminium ion, which appears to be instantaneous. Two simple experiments gave a clear idea of the equilibria concerned. A solution of amino ether in acid (iminium ion) was prepared, and one part neutralized to phenolphthalein, while another was made strongly alkaline. Each was then *rapidly* acidified. In the first case only about 15% of the original iminium ion was recovered, but in the second over 90% was found. A similar pair of experiments which differed in that the alkaline solutions were *slowly* acidified yielded, in both cases, a smaller amount of iminium ion, about five per cent. Identical results were obtained by starting with solutions of formaldehyde and diethylamine in equal molal ratio. The reaction is therefore strictly reversible. In dilute solution the amino alcohol corresponds at equilibrium to more than 80% of the theoretical.<sup>7</sup>

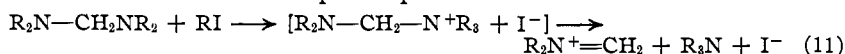
**Discussion of Results.**—Referring to Equation (10) below, slow addition of acid neutralizes the secondary amine and gradually shifts the equilibrium to the left, suggesting that diethylamine is a stronger base than the amino alcohol. Strong alkali shifts equilibria C and B to the right, the equilibrium A to the left. Experimentally, rapid acidification of this alkaline solution produces the iminium ion, which means either that the equilibrium A is more rapidly established than equilibrium C, resulting in loss of hydroxide ion rather than secondary amine, or that hydrogen ion first adds to form the ion,  $R_2N^+H-CH_2-OH$ , which then loses water rather than dialkylammonium ion. We are inclined to the first view, since the quaternization of the nitrogen, as mentioned in a footnote above, tends to stabilize negative groups in the alpha position.



<sup>7</sup> Henry, *Bull. Acad. Roy. Belgique*, [3] **28**, 370 (1894), claims to have isolated  $\alpha$ -amino alcohols of the type  $R_2N-CH_2-OH$  by the action of formaldehyde on secondary amines. His procedure normally leads to  $\alpha$ -amino ether if alcohol is present, or to the methylenediamines if it is absent. He had no satisfactory criterion of purity and whereas it is believed that the simple amino alcohols exist in dilute aqueous solution, it is felt that any attempt to concentrate or dehydrate them results in the formation of methylene diamines or the diaminodimethyl ethers.

Step C is the rate determining step for the formation and molecular dissociation of the pseudo base. The conclusion is drawn that step A is much faster than steps B and C taken as successive reactions.

The chemistry of the substituted methylenediamines gives support to this mechanism. Attempts to quaternize them fail<sup>8</sup>



Solution in acid produces the iminium ion<sup>9</sup>



The difficulty experienced in producing the iminium ion quantitatively from the amino ethers, methylenediamine or the polyiodide may be entirely due to a heterogeneity factor. The iminium ion is first formed in the boundary region between the acidic solution and the added amino ether; it can then pass to the acidic region and be metastable, or it can be subjected to alkali (or low acidity) in the adjoining region and be rapidly converted to amine and aldehyde.

### Experimental Part

**Preparation of Substituted Aminomethyl Ethers and Methylenediamines.**—The method of McLeod and Robinson,<sup>1,3</sup> was modified in order to eliminate the presence of large amounts of excess formaldehyde in the crude product.

**Diethylaminomethyl Methyl Ether.**—Seventy-four grams of diethylamine was added to 34 g. of methyl alcohol; 30 g. of paraformaldehyde was added and the mixture placed under a reflux condenser. An ice-bath was kept in readiness as the reaction becomes quite vigorous and must be slowed down. When the reaction had ceased, anhydrous potassium carbonate was added and the whole allowed to stand overnight. The potassium carbonate was then filtered off by suction and the filtrate fractionated. A fraction distilling at 114–120° (755 mm.) was collected and dried with metallic sodium. Refractionation yielded 47 g. of a colorless, mobile liquid boiling at 115–115.8° (755 mm.). A sample of the product was dissolved in 10 cc. of ethyl alcohol and titrated with 0.1000 normal hydrochloric acid, using methyl orange as an indicator. An equivalent weight of 118.0 was obtained: calcd. for C<sub>6</sub>H<sub>15</sub>ON, 117.1; yield, 40%.

The same general method outlined above was used in the preparation of all the aminomethyl ethers listed below.

**Diethylaminomethyl Ethyl Ether.**—Seventy-three grams of diethylamine, 80 g. of ethyl alcohol (95%) and 30 g. of paraformaldehyde yielded 90 g. of a colorless, mobile liquid boiling at 132–134° (756 mm.). The equivalent weight was determined as 131.0: calcd. for C<sub>8</sub>H<sub>17</sub>ON, 131.1; yield, 69%.

<sup>8</sup> Litterschied, *Ann.*, **335**, 368 (1904), isolated the unstable dimethiodide of the furfuraldehyde derivative.

<sup>9</sup> Knoevenagel and Mercklin, *Ber.*, **37**, 4087 (1904), claimed to have prepared the dihydrochloride salt of the substituted methylenediamine. Attempts to repeat the preparation in dry alcoholic and ethereal chloride gave us only diethylamine hydrochloride. Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887), states that he was unable to obtain the dihydrochloride of the tetraethyl derivative, but did obtain the platinum double salt of the tetraisobutylmethylenediamine. We believe that we have shown that the substance he obtained has the structure [CH<sub>2</sub>=N(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>]<sub>2</sub>PtCl<sub>6</sub>. See also Branch, *This Journal*, **38**, 2466 (1916).

**Diethylaminomethyl *n*-Butyl Ether.**—Seventy-five grams of diethylamine, 95 g. of *n*-butyl alcohol and 30 g. of paraformaldehyde yielded 114 g. of a colorless, mobile liquid boiling at 172–173° (758 mm.). The equivalent weight was determined as 159.0: calcd. for  $C_9H_{21}ON$ , 159.2; yield, 72%.

**Diethylaminomethyl *n*-Heptyl Ether.**—Forty grams of diethylamine, 105 g. of *n*-heptyl alcohol and 15 g. of paraformaldehyde yielded a colorless liquid boiling at 112.5° (15 mm.). The equivalent weight was determined as 303.0: calcd. for  $C_{12}H_{27}ON$ , 201.2.

**Di-*n*-propylaminomethyl *n*-Butyl Ether.**—Sixty grams of di-*n*-propylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded 74 g. of a colorless, mobile liquid boiling at 87° (42 mm.). The equivalent weight was determined as 185.7: calcd. for  $C_{11}H_{25}ON$ , 187.2; yield, 79%.

**Diisopropylaminomethyl *n*-Butyl Ether.**—Ten grams of diisopropylamine, 14 g. of *n*-butyl alcohol and 2.9 g. of paraformaldehyde were mixed as already described. No attempt was made to purify the compound.

**Di-*n*-butylaminomethyl *n*-Butyl Ether.**—Seventy grams of di-*n*-butylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 116° (11 mm.).

**Diisobutylaminomethyl *n*-Butyl Ether.**—Seventy-five g. of diisobutylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded 88 g. of a colorless, mobile liquid boiling at 92° (5 mm.). The equivalent weight was determined as 213.5: calcd. for  $C_{13}H_{29}ON$ , 215.2; yield, 82%.

**Di-*n*-amylaminomethyl *n*-Butyl Ether.**—Eighty grams of di-*n*-amylamine, 70 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 128° (5 mm.).

**Methylphenylaminomethyl *n*-Butyl Ether.**—Fifty-five grams of methylaniline, 70 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde were mixed as already described. The mixture was fractionated under reduced pressure. Everything distilling over above 110° (10 mm.) was used.

**Diallylaminomethyl *n*-Butyl Ether.**—Fifty grams of diallylamine, 70 g. of *n*-butyl alcohol, and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 89° (11 mm.).

***n*-Butoxymethylpiperidine.**—Eighty grams of piperidine, 100 g. of *n*-butyl alcohol and 30 g. of paraformaldehyde yielded a colorless liquid boiling at 82° (5 mm.).

**Dimethylaminomethyl *n*-Butyl Ether.**—Twenty-five grams of dimethylamine, 70 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 128° (756 mm.). The equivalent weight was determined as 132.5: calcd. for  $C_7H_{17}ON$ , 131.1.

**Tetraethylmethylenediamine.**<sup>10</sup>—One hundred fifty grams of diethylamine and 30 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 166–167 (757 mm.); 128 g. of material was obtained. The equivalent weight was determined as 80.0: calcd. for  $C_8H_{22}N_2$ , 79.1.

**3-β-Hydroxyethylloxazolidine.**—Ten grams of diethanolamine, 14 g. of *n*-butyl alcohol and 2.8 g. of paraformaldehyde were mixed in an attempt to prepare diethanolaminomethyl *n*-butyl ether. Fractionation yielded a colorless viscous liquid boiling at 78° (2 mm.). The equivalent weight determined by titrating with *N*/10 hydrochloric acid was 119.5. The equivalent weight of the material was also determined by means of bisulfite and iodine, and found to be 65.3. The molecular weight, calculated for  $C_6H_{11}NO_2$ , is 117.1. Further purification was not attempted.

**The Reaction between the Amino Ether or Methylenediamine and Paraformaldehyde.**—Solid paraformaldehyde was stirred with a quantity of diethylaminomethyl-*n*-

<sup>10</sup> Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887).

butyl ether in a closed system for several days. Samples were withdrawn through a filter at intervals and the equivalent weight determined by acidic titration. The paraformaldehyde appeared to be practically insoluble as such. The amino ether added one mole of formaldehyde within ten days at 30°, after which the reaction proceeded much more slowly. The product was not investigated in detail, except to observe that it was high boiling and that its formation was to some extent reversible. It is probably a simple addition product such as diethylaminomethyl *n*-butoxymethyl ether.

In a similar way *N*-tetraethylmethylenediamine added formaldehyde. The reaction was practically complete in five days. Figure 1, in which the equivalent weight of the liquid phase of the reaction mixture is plotted against the time, illustrates this difference in rate. The formation of this type of addition product is the reason for avoiding the presence of excess formaldehyde during the preparations. On the other hand, in the preparation of the amino ether a large excess of diethylamine is to be avoided, since the *N*-tetraethylmethylenediamine will be formed and is difficult to separate by fractionation.

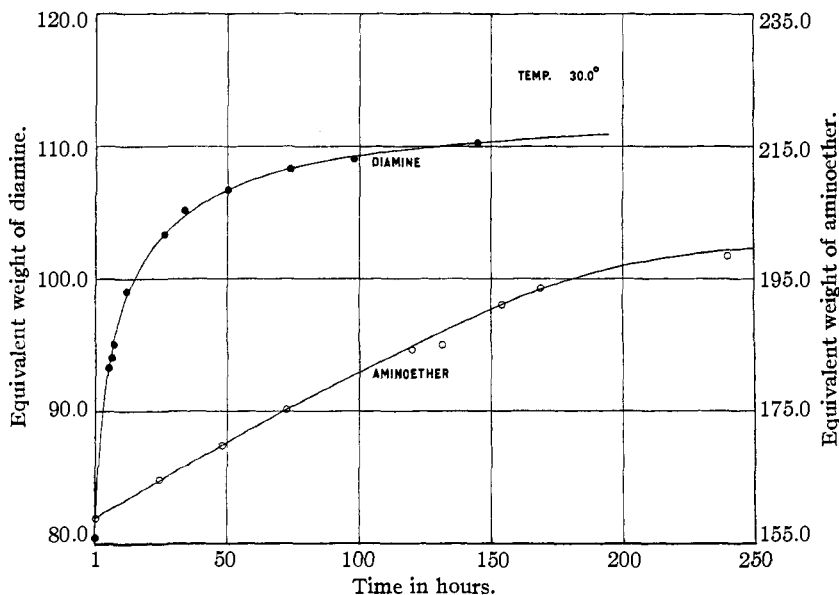


Fig. 1.—The addition of formaldehyde to the amino ether and methylenediamine, temp. 30°.

**Preparation and Iodine Titration of Sodium-*N*-diethylaminomethyl Sulfonate.**—Knoevenagel and Mercklin's method of preparation<sup>11</sup> was modified slightly. Solid formaldehyde sodium bisulfite was precipitated from a concentrated solution by alcohol and the dry salt redissolved in half its weight of water. Slightly in excess of one mole of liquid diethylamine was added slowly and the mixture placed in a desiccator. After a few hours standing the sample was dried *in vacuo* over calcium chloride. A weighed sample was dissolved in *N*/10 hydrochloric acid and the solution titrated with standard sodium hydroxide to the methyl orange end-point. The end-point was obscure; the indicated equivalent weight was  $200 \pm 5$ , the theoretical 189.1. A similarly prepared

<sup>11</sup> Knoevenagel and Mercklin, *Ber.*, **37**, 4087 (1904).

acid solution was titrated with iodine. From one to two per cent. (0.3 cc.) of the iodine was used up rapidly, the remainder (19.7 cc.) was used up slowly. The equivalent weight on the basis of the total iodine was  $97 \approx 1$ . The method of preparing the solution and its time of standing affected the results. The dry salt was stable for months.

The rate of the slow titration with iodine was ascertained to be first order in the aminosulfonate concentration and independent of the iodine concentration. It was markedly affected by temperature, slightly by changing ionic strength with small specific ion effects (retarded by iodide, increased by sulfate ion) and very slightly affected by changing hydrogen-ion concentration in the region of one-tenth normal. The usual plot,  $\log(\text{reactant})$  against time, was a straight line. In two identical experiments, except that in one the iodine was added in 1.0-cc. portions and the color allowed to fade, and in the other iodine was added drop by drop, keeping a barely perceptible color present (no starch), the specific rate constants at  $25.0^\circ$  were, respectively,  $1.603 \times 10^{-3}$  and  $1.592 \times 10^{-3} \text{ sec.}^{-1}$ . After the completion of the reaction, a solution of sodium bisulfite equivalent to the iodine used in slow titration was added, and the titration repeated immediately after mixing. The same rate was observed as before for all the sulfite, within one per cent.

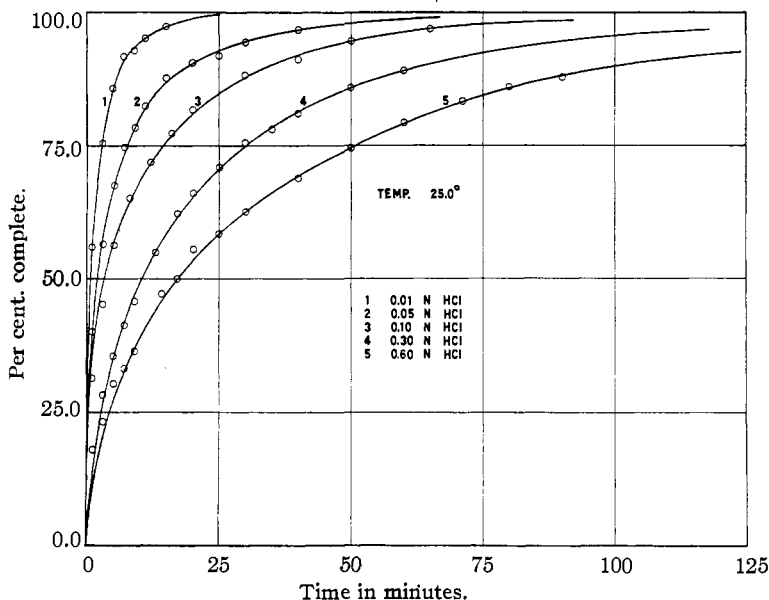


Fig. 2.—The addition of bisulfite ion (0.0366 *M*) and formaldehyde (0.0366 *M*).

**Rate of Addition of Bisulfite to Formaldehyde as a Function of Hydrogen-Ion Concentration.**—For control purposes the data plotted in Fig. 2 were obtained by adding aqueous formaldehyde and sodium bisulfite solutions to hydrochloric acid solutions, and following the disappearance of the ionized sulfite with iodine in extracted samples.

**Formation of the Periodide,  $\text{CH}_2=\text{N}^+\text{R}_2\text{I}_3$  or  $\text{CH}_2(\text{I})\text{NR}_2(\text{I}_2)$ .**—Addition of excess iodine to a solution of the iminium ion, preferably by oxidizing part of the iodide ion present by iodate ion, produces an oily precipitate of about the consistency of mercury. This was washed with aqueous potassium iodide solution until the ratio of nitrogen to iodine in the washings approached that ratio in the oil. The first washings contained



excess iodine. The periodide analyzed as follows: by the Carius method, using sugar as a reducing agent, 0.3790 g. gave 0.6201 g. of AgI, or 88.4% I; calculated for  $I-CH_2-N(C_2H_5)_2I_4$ , 88.1%. By Kjeldahl, 0.3580 g. gave 0.0072 g. N or 2.02%; calculated, 1.94%. Dissolved in 20 cc. of acidified alcohol (2.0 cc. 1.0 *N* HCl) and titrated with 0.1000 *N* thiosulfate, 0.3580 g. used 19.70 cc., an equivalent weight of 182; calculated, 180. To the resulting solution a known amount of sodium bisulfite solution was added, and after one minute the *excess* ionized sulfite was titrated rapidly; sulfite used up,  $9.9 \times 10^{-4}$  equivalents; calcd.,  $9.95 \times 10^{-4}$  equivalents;  $d_{20}^{20}$  2.81. Excess of iodide ion dissolves (or prevents the formation of) the polyiodide. The formulas assigned are arbitrary, but there is one good reason to prefer the second in comparison to the first above. On the basis of the first formula, the reactions of the iodine should not affect the iminium ion. However, great difficulty was experienced in regenerating that ion from the substance, particularly when the insoluble oil was shaken with aqueous solutions of iodide, sulfite or thiosulfite. In nearly every case most of the compound appeared as formaldehyde or formaldehyde bisulfite addition product. The solution in acidified alcohol, described above, sometimes failed to give a quantitative yield of the iminium ion. The most trustworthy procedure for analytical purposes involved solution of the oil in acidified alcohol and addition of excess bisulfite.

**Preparation of a Solution of N-Diethylmethyleiminium Salt.**—Diethylamino-methyl isobutyl ether (0.4312 g.) was added dropwise with vigorous stirring to 3.00 cc. (0.29 cc. excess) of 1.0 *N* hydrochloric acid. To this solution 40.00 cc. of sodium bisulfite solution, equivalent to 64.00 cc. of 0.1000 *N* iodine, was added. Titration with iodine used 10.10 cc. of 0.1000 *N* iodine rapidly, to a fading end-point which could be measured to better than 0.1 cc. More iodine solution was then added until the end-point became permanent. This required about ninety minutes and used 53.7 cc. or a total of 63.8 cc. of iodine. The 0.2 cc. loss was probably due to the formation of formaldehyde bisulfite in small amount, which does not titrate with iodine in acid solution. Using the fading end-point as the proper measure of the amount of sulfite reacted, the equivalent weight of the amino ether to this reaction is 80.0. Toward direct titration with acid another sample gave an equivalent weight of 159.2. The production of the iminium ion was nearly quantitative.

Adding the original reagents in the inverse order, or not stirring so vigorously, or using 0.1 *N* acid, gave poorer yields.

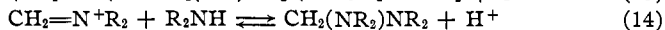
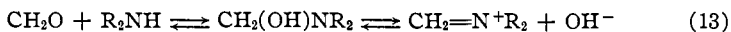
**Mechanism.**—To show that after solution of the amino ether in acid the reactive species was the iminium ion, the following experiments were made: 0.00278 mole of the isobutyl ether was dissolved in 0.0035 equivalent to 1.0 *N* acid as before. The solution was evaporated *in vacuo* through a liquid-air trap to two-thirds its volume. The trap contained two liquid layers after warming, with the marked odor of isobutyl alcohol. The alcohol was taken up in benzene, the solution dried and the alcohol esterified with 2.0 cc. of acetic anhydride; 0.00197 equivalents of alcohol, amounting to a 65% yield, was found. The residue was treated with bisulfite (0.0060 equiv.) as before and the fading and permanent end-points to iodine noted. The slow titration involved 0.00557 equivalents of iodine or practically 100% yield of iminium ion. Hence the sulfite compound could not all have been formed from the ether directly. This result was obtained by avoiding too dilute solutions and allowing only two and one-half hours for the distillation.

An acidified solution of diethylammonium chloride, formaldehyde and bisulfite when titrated with iodine, gave no fading end-point and used the full amount of iodine solution expected on the basis of the sulfite present.

**Isolation of the Crystalline Salt.**—2.715 grams of the isobutyl ether derivative was titrated rapidly at room temperature to the methyl orange end-point with 1.00 *N*

hydrochloric acid. The solution was evaporated *in vacuo* over calcium chloride as rapidly as possible and yielded hygroscopic, white crystals. *Anal.*: 0.5500 g. in 0.10 *N* acid used 0.00478 equivalent of sulfite and produced by Kjeldahl 0.00242 equivalent of ammonia; equivalent weight to sulfite, 115, to Kjeldahl, 227.0; calcd. for  $\text{CH}_2=\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}\cdot 6\text{H}_2\text{O}$ , 229.5. The remainder of the preparation stood in the desiccator over calcium chloride for several weeks. A 0.1589-g. sample was dissolved in 0.1 *N* acid and 0.002340 equivalent of bisulfite added; iodine used up to the fading end-point was 0.00072 equivalent, to the permanent end-point 0.00162 equivalent. When treated by the Kjeldahl process, the sample gave 0.000828 equivalent of ammonia: equivalent weight, to sulfite, 98; to Kjeldahl, 192; calcd. for  $\text{CH}_2=\text{N}(\text{C}_2\text{H}_5)_2\text{Cl}\cdot 4\text{H}_2\text{O}$ , 193.5. Another sample was allowed to stand longer in the presence of the excess sulfite to permit any free formaldehyde in the sample to react, as shown by failure subsequently to titrate completely all the bisulfite added. No evidence of any formaldehyde could be found. Since the remaining possible impurity, diethylammonium chloride, could not be present without throwing out the ratio of the two equivalent weights as determined above, it is presumed that water of crystallization is present. No further examination of the product was made. Repeated attempts to duplicate the preparation failed. Its original success was probably due to a fortuitous use of the proper amount of hydrochloric acid, since excess acid hastens the rate of hydrolysis to formaldehyde, while a basic solution produces a very rapid decomposition of the iminium ion to formaldehyde and secondary amine.

**The Reaction between Formaldehyde and Diethylamine in Dilute Aqueous Solution.**—These reagents could form the simple amino alcohol (pseudo base) by addition, or the methylenediamine derivative, or the iminium hydroxide.



Any one or all of these products upon *rapid* acidification could yield the substituted iminium ion. Slow acidification definitely produces only a trace of iminium ion. Acidification of the amine before adding formaldehyde permits no iminium ion to form; in fact, the latter is slowly hydrolyzed in acid at room temperature to the aldehyde and amine salt, so must be considered unstable in this medium. Since the iminium ion can be detected quantitatively by the sulfite reaction as explained above, some idea as to the molecular species present can be obtained. Table I describes a few experiments in which equal volumes (100 cc.) of amine and formaldehyde solutions were mixed, with and without the addition of acid or alkali. The last column gives the per cent. of total amine present, which is in the form of iminium ion after acidifying very rapidly. In the

TABLE I  
THE REACTION BETWEEN FORMALDEHYDE AND DIETHYLAMINE

Expt.	Formaldehyde concn., m./l.	Diethylamine concn., m./l.	Acid or Base (6 <i>N</i> ), cc.	Iminium ion. per cent. of total amine
1	0.18	0.4	5.7 (acid)	10
2	.18	.13	...	85
3	.20	.20	...	92
4	.20	.20	4.0 (base)	96

sample partly neutralized by acid (Expt. 1), the iminium ion formation corresponded to about 10% of the free amine present; in the others it approximates complete reaction. This indicates the formation of the amino alcohol or iminium base, since the diamine could yield as a maximum only 50% of iminium ion. This was further tested by freezing point determinations.

The freezing point lowering of a given 0.18 *M* formaldehyde solution was 0.311°. If the formaldehyde was not polymerized and formed a perfect solution, it would have been 0.334°. Anhydrous diethylamine was added sufficient to bring its concentration to 0.044 *M*. The freezing point lowering was then 0.316°. The amine concentration was raised to 0.126 *M*; and the freezing point lowering became 0.367°. Assuming 85% conversion of the amine to the amino alcohol, the freezing point lowering should have been 0.370°. These figures show qualitatively that one mole of addition product results, and together with the fact of 90% conversion to iminium ion in acid solution, point to the undissociated pseudo base,  $\text{CH}_2(\text{OH})\text{NR}_2$ , as the main product. Equation (13) above best represents these facts, in which the first equilibrium is shifted to the left by acid and to the right by strong base. Action of acid upon the pseudo base leads first to the rapid formation of iminium ion, followed by the slower establishment of the equilibrium corresponding to the new alkalinity of the solution. If the addition of acid results in an acid solution, the metastable iminium ion is formed.

**The Reaction between Aqueous Acid and Tetrasubstituted Methylenediamine.**—The equivalent weight of freshly distilled, sodium-dry tetraethylmethylenediamine was determined as 80.0 by titration with *N*/10 hydrochloric acid; 0.3040 g. of this diamine was then added dropwise to 20.0 cc. of *N*/1 hydrochloric acid using a mechanical stirrer. Then 42.65 cc. of sodium bisulfite (equivalent to 39.10 cc. of 0.1008 normal iodine) and 2.0 cc. of starch solution were added and the solution immediately back-titrated with iodine; 3.05 cc. of 0.1008 normal iodine was added to the fading end-point and a total of 38.80 cc. of iodine to the permanent end-point. The equivalent weight of the diamine, on the basis of this titration, is 83.7. The equivalent weight calculated for  $\text{C}_9\text{H}_{22}\text{N}_2$  is 79.1.

***N*-Diisobutylmethyleiminium Chloroplatinate.**—Diisobutylaminomethyl *n*-butyl ether was dissolved rapidly in a small excess of *N* hydrochloric acid, and chloroplatinic acid added. The light yellow precipitate was filtered off, washed with water and alcohol and dried in a desiccator. It melted with decomposition (heating started at room temperature) at 196–197° and 0.0579 g. gave 0.0161 g. of Pt: found, 27.8% Pt; calcd. for  $[\text{CH}_2=\text{N}(\text{C}_4\text{H}_9)_2]_2.\text{PtCl}_6$ , 28.2%. Ehrenberg<sup>12</sup> obtained a platinum salt from the corresponding diamine which decomposed at the same temperature and contained 28.35% Pt. He assigned to it the formula,  $\text{CH}_2(\text{N}(\text{C}_4\text{H}_9)_2\text{H})_2\text{PtCl}_6$ , but it corresponds in all respects to the above substance, which cannot be of the structure assigned by Ehrenberg. Diisobutylammonium chloroplatinate melts at 212–213°, with decomposition and contains 29.21% platinum. It is the most probable impurity.

<sup>12</sup> Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887).

### Summary

1. The preparation of a number of dialkylaminomethyl ethers is described.

2. The mechanism of their hydrolysis to formaldehyde, alcohol and secondary amine has been studied and the conclusion reached that it involves the primary formation of N-dialkylmethyleneiminium ion, which subsequently adds hydroxide ion to yield the amine and formaldehyde.

3. N-Diethylmethyleneiminium chloride,  $(C_2H_5)_2N=CH_2Cl \cdot 6H_2O$  has been isolated. The platinum double salt,  $(iso-C_4H_9)_2N=CH_2)_2PtCl_6$ , has been prepared from the corresponding amino ether. It corresponds to the platinum double salt of Ehrenberg, prepared from tetraisobutylmethylene diamine.

4. The reaction between formaldehyde and diethylamine in dilute aqueous solution has been studied to confirm the mechanism of reaction of the amino ethers.

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

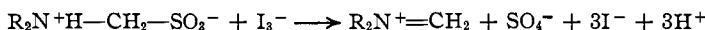
## THE RATE OF REACTION OF DISUBSTITUTED AMINOMETHYL SULFONIC ACIDS WITH IODINE

BY T. D. STEWART AND WILLIAM E. BRADLEY

RECEIVED JUNE 14, 1932

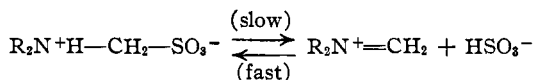
PUBLISHED NOVEMBER 5, 1932

The substituted aminomethyl sulfonic acids react with iodine in acid solution according to the equation



It has already been observed<sup>1</sup> that the reaction rate is independent of the iodine concentration, even for very low concentrations of iodine, and is first order with respect to the aminosulfonic acid. The rate is affected slightly by salts; the effect of increasing hydrogen-ion concentration up to about tenth normal is to decrease the rate; beyond that, up to one normal, there is but a small effect. At very low acidity the reaction is very fast and little or no iminium ion is formed.

The rate determining step appears to be the rate of ionization, represented as



The free sulfite ion at equilibrium is less than one per cent. In fairly concentrated solutions some indication of the dissociation is found. The reaction would appear to lend itself peculiarly well therefore to a study

<sup>1</sup> Stewart and Bradley, *THIS JOURNAL*, **54**, 4172 (1932), discuss this reaction and the evidence for the iminium ion.