range of temperature from −22.5 to 223° is now covered.

2. The amount of nitrogen produced exceeds the amount of hydrocarbon gas. The discrepancy increases to a maximum at about 200°.

3. The amount of higher hydrocarbon produced (presumably propane) increases with increase in temperature. The amounts of hydrogen and unsaturated hydrocarbon produced are generally negligible.

4. The results substantiate the suggestion previously made that there is a secondary association reaction between free radicals and azomethane.

5. A recalculation of quantum yield data in the literature, on the basis of the analyses here reported, casts doubt on the validity of the conclusion that the temperature coefficient of the photolysis at temperatures $<226°$ is zero.

6. The results indicate that estimates of chain length initiated by azomethane would at best be minimum values.[11]

[11] Through a typographical error in THIS JOURNAL, **59**, 1044 (1937), we are made to say the opposite to this. The line in the middle of the second column should read ". . . since fewer but longer chains would *now* be required to explain the effects observed."

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NEW YORK, N. Y.

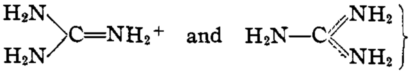
RECEIVED JULY 1, 1937

[CONTRIBUTION NO. 153 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in the Urea Series. XIV.[1] Structure of the Guanidonium Ion, Evidence from Electrolysis[2]

BY TENNEY L. DAVIS, WILLIAM E. YELLAND AND CHUK-CHING MA

The fact that guanidonium hydroxide is an extremely strong base, indistinguishable from potassium hydroxide in electrometric titration,[3] suggests that the guanidonium ion is not of the ammonium type, that guanidine owes its salt-forming properties to some cause other than its being a substituted ammonia. A comparison of the basicities of various alkyl-substituted guanidines and a study of the behavior of these substances on nitration[4] show definitely that the salt-forming properties of these bases cannot be attributed to any particular one of the three nitrogen atoms which each of them contains. The perfect stability of guanidonium nitrite in boiling aqueous solution[5] is not a property of a nitrite of an ammonium base. Edsall,[6] from Raman spectrum measurements, recently has concluded that the guanidonium ion possesses trigonal symmetry and contains three amino groups attached to the central carbon atom. Some years ago Madelung[7] formulated guanidonium hydrochloride $[C(NH_2)_3]^+Cl^-$, considered it to be a carbonium salt and compared it in an interesting manner with pararosaniline hydrochloride—which he formulated $[C(C_6H_4NH_2)_3]^+Cl^-$—pointing out that carbonium salts are not necessarily colored and that pararosaniline hydrochloride owes its color rather to the phenylene groups by which the amino groups are attached to the central carbon atom. Lecker and Graf[8] in consequence of their study of peralkylated guanidines concluded that guanidonium salts contain three amino groups (or six hydrogen atoms capable of being replaced by alkyl groups), but judged that the position of carbon in the periodic table made it unlikely that it would have a positive function and supposed the charge to be resident upon one of the nitrogen atoms. They assigned to the guanidonium ion two formulas which they regarded as identical, namely



$$\begin{matrix}H_2N\\H_2N\end{matrix}\!\!>C{=}NH_2^+ \quad \text{and} \quad \left.H_2N{-}C\!\!\begin{matrix}NH_2\\NH_2\end{matrix}\right\}^+$$

While the discharge of such ions might be expected to yield guanidine and hydrogen, we find that hydrogen is not a primary product of the electrolysis and that there is no evidence of a doubling up, through a nitrogen–nitrogen linkage, of molecules of this type. Indeed the products which we find are not those which would be expected from the discharge of an ammonium type ion or of any other in which the charge is resident upon a nitrogen atom, but are those which would be expected if the guanidonium ion is the

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[1] No. XIII of this series, THIS JOURNAL, **58**, 1800 (1936).

[2] Paper read before the Organic Chemistry Division, A. C. S., at the meeting at Rochester, New York, September 7, 1937.

[3] Davis and Elderfield, THIS JOURNAL, **54**, 1499 (1932).

[4] Davis and Elderfield, *ibid.*, **55**, 731 (1933).

[5] Davis and Abrams, *Proc. Am. Acad. Arts Sciences*, **61**, 444 (1926).

[6] Edsall, *J. Phys. Chem.*, **41**, 133 (1937).

[7] Madelung, *Ann.*, **427**, 35 (1922).

[8] Lecker and Graf, *ibid.*, **438**, 154 (1924); **445**, 61 (1925).

triamino-carbonium ion having its positive charge upon the central carbon atom.

No discussion of the electrolysis of guanidonium salts appears to exist in the literature. If the electrolysis is carried out with a platinum anode and a mercury cathode, gassing occurs at both electrodes, the solution becomes ammoniacal, and the mercury, or at least the surface of it, is converted slowly into an amalgam. When the current is shut off, the amalgam collapses rapidly while evolution of gas from the surface of the mercury continues for a short time. We have thought that information concerning the nature of the amalgam, and concerning the source of the ammonia—whether from the decomposition of a guanidonium amalgam, from the reduction of guanidine, or from the discharge and subsequent decomposition of the ion—would throw light upon the structure of the guanidonium ion.

If the guanidonium ion were of the ammonium type, it might be expected to yield an amalgam. Le Blanc[9] in 1890 by polarization measurements demonstrated that ammonium amalgam is electronegative for ten or fifteen minutes with respect to the solution from which it has been prepared, and presented similar evidence for the existence of monomethyl-, dimethyl-, tetramethyl-, and diethyl-ammonium amalgams but did not isolate the amalgams in question. McCoy and his co-workers[10] have produced tetramethyl- and monoethyl-ammonium amalgams by the electrolysis of the chlorides in absolute alcohol at −10°, silver white crystalline solids, stable at 0° but decomposing above that temperature, stable in contact with absolute alcohol at 0° but reacting violently with water. They measured the potentials of the cells, amalgam/0.5 N chloride/0.1 M calomel/mercury, both with absolute alcohol and with water, and found for the monoethyl-ammonium amalgam in water 2.4 volts, in alcohol 1.9 volts, for tetramethylammonium amalgam in water 2.4 to 1.7 volts, in alcohol 2.6 to 2.0 volts. They considered the range of voltage to be due to the fact that the amalgam consisted of more than one phase. They investigated eighteen other organic chlorides but were unable to isolate any other amalgams.

By electrolysis at −30 to −40° of solutions of guanidonium sulfate in dry methyl and ethyl alcohol, ethylene glycol, and glycerol, and of guanidonium acetate and chloride in dry methyl alcohol, we have obtained amalgams, pasty masses which contained no solid crystals and which, washed and freed from solution, decomposed with the production of ammonia and hydrogen—and in all respects behaved like ammonium amalgam. When the electrolysis of guanidonium sulfate in water or in alcohol was carried out at laboratory temperature, the mercury cathode swelled up and took on a lumpy appearance but collapsed immediately when the current was discontinued. We conclude that dilute ammonium amalgams are formed under these conditions.

Polarization measurements were made on a mercury electrode in contact with a 0.1 N solution of guanidonium sulfate in water at 0°. The mercury was made the cathode for electrolysis (0.1 ampere); the electrolyzing current was then shut off, and the electrode and solution were made part of a potentiometer circuit through a bridge filled with 0.05 M sulfuric acid and a mercuric sulfate in 0.05 M sulfuric acid/mercury half cell. The alternations between the electrolyzing circuit and the potentiometer circuit were made with a frequency of 1140 times per minute by means of a rotating switch. In several experiments the potentiometer readings commenced at about 2.7 volts and fell more or less steadily to a value of approximately 0.7 volt in about fifteen minutes. In each case the experiment had to be stopped because of the swelling and gassing of the mercury electrode. When the electrolyzing current was shut off wholly, the potentiometer readings dropped in two or three minutes to a value of 0.13 to 0.30 volt which was the same as the reading before the electrolysis was begun, a result which indicates that the amount of the ammonium amalgam on the surface of the mercury electrode was very small. The dropping potentiometer readings during these experiments evidently are to be explained by the consideration that the solutions, originally 0.1 N in guanidonium sulfate, contained less guanidonium and more ammonium and ammonia as the experiments advanced, and the small amounts of the ammonium amalgam by the consideration that the electrolytes contained far fewer ammonium ions than they would, say, if they were 0.1 N in ammonium sulfate. Similar experiments were carried out in which 0.1 N ammonium sulfate and

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[9] Le Blanc, *Z. physik. Chem.*, **5**, 467 (1890).

[10] McCoy and Moore, THIS JOURNAL, **33**, 273 (1911); McCoy, *Science*, **34**, 138 (1911); McCoy and West, *J. Phys. Chem.*, **16**, 260 (1912).

0.1 *N* potassium sulfate were used instead of the 0.1 *N* guanidonium sulfate. More lasting amalgams were formed. When ammonium sulfate was used, the potentiometer readings during the electrolysis increased regularly from about 0.8 to about 1.0 volt; after the electrolyzing current was shut off, they were fairly constant at about 1.4 volts for more than twenty minutes. When potassium sulfate was used, the readings were about 0.9 to 1.0 volt, and about 1.2 volts, respectively. The results of the polarization measurements are what would be expected if the amalgam which is formed during the electrolysis of guanidonium salts is a dilute ammonium amalgam formed from ammonia produced in the electrolyte by the action of the current on the guanidonium salt.

The hypothesis that hydrogen at the cathode reduces guanidine to triaminomethane, and that this substance breaks down into ammonia and formamidine, the formamidine being hydrolyzed to additional ammonia and formic acid, is untenable for the reason that formic acid could not be detected in the solution. Moreover, no means of reducing guanidine is known. We find that guanidonium carbonate and sulfate are unaffected by the usual methods of catalytic hydrogenation in water and in alcohol, respectively. It seems necessary to suppose that the ammonia produced during the electrolysis arises, not from the reduction, but from the discharge of the guanidonium ion.

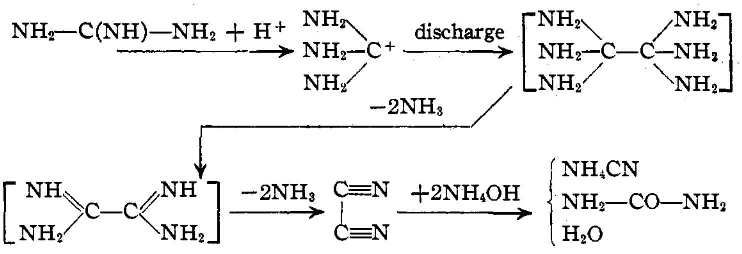
The hypothesis that the guanidonium ion is of the ammonium type, $NH_2—C(NH)—NH_3^+$, and that this breaks, by a sort of dearrangement at the moment of its discharge, into ammonium which amalgamates (or into ammonia and hydrogen) and cyanamide, is excluded by the fact that cyanamide could not be detected in the solution.

Moreover, both of these hypotheses fail to account for the substances which actually are found to be produced in the electrolyte.

A solution of guanidonium carbonate was electrolyzed in a Hoffman apparatus with a mercury cathode and a platinum anode, and the gases were removed at regular intervals and analyzed. After the current had been passing for a short time, the volume of the cathode gases (mostly hydrogen) was actually less than the volume of the anode gases (mostly oxygen). As the electrolysis continued, the ratio increased, and, after a considerable period of electrolysis, the volume of the cathode gases was increasing about three times as fast as the volume of those from the anode. This fact seems difficult to interpret but can be explained by supposing that hydrogen is in some way either consumed during the early stages of the electrolysis, or is not produced at that time, and that oxygen is consumed during the later ones. The gases from both electrodes contained considerable nitrogen, but no ammonia and no hydrocarbons. The liquid in the cathode compartment was strongly ammoniacal. An experiment with a platinum cathode gave the same gases as when a mercury electrode was used.

A solution of guanidonium carbonate was electrolyzed in a two-compartment cell, a mercury cathode in the outer vessel and a platinum anode in the porous cup. One and one-half times the theoretically required amount of current was passed. Considerable transference of solvent occurred, so that at the end of the experiment the volume of the anode liquid in the porous cup was reduced greatly. This liquid was acidic, and on distillation yielded a liquid which smelled strongly of prussic acid and gave a qualitative test for cyanide. The strongly ammoniacal cathode liquid gave no test for cyanide. Neither liquid gave any test for formic, oxalic, or cyanic acid, biuret, or cyanamide. Both liquids were evaporated to dryness and the residues extracted with acetone, in which guanidonium carbonate is insoluble, and the acetone extracts, evaporated and recrystallized from butanol, yielded urea. The electrolysis of 35 g. of guanidonium carbonate in this way gave from the cathode compartment 1.9 g. of urea, from the anode compartment 0.15 g. of urea, identified by mixed melting point with a known sample and by melting point and mixed melting point of its di-*p*-tolyl derivative. The electrolysis of 30 g. of guanidonium sulfate similarly gave 1.7 g. of urea from the cathode compartment and a very small amount from the anode compartment.

The simultaneous production of urea and cyanide during the electrolysis of guanidonium salts suggests the temporary presence or intermediacy of cyanogen, and gives plausibility to the belief that the guanidonium ion is the triamino-carbonium ion, a belief which also accounts for the other phenomena observed during the electrolysis. The triamino-carbonium ion, discharged at the cathode, evidently doubles up to produce the unstable hexaaminoethane, which, through loss of ammonia, yields cyanogen as indicated below.



The ammonia remains in the liquid of the cathode compartment and accounts for the ammonium amalgam which is formed. The cyanogen reacts promptly with the ammonium hydroxide to form cyanide and cyanate ions. The electronegative cyanide ions migrate to the anode. In the presence of ammonia the cyanate ions have no more than a most momentary existence: they unite with the ammonia to form urea which is un-ionized and remains for the most part, or perhaps wholly, in the cathode compartment where it has been found in largest amount. No hydrogen is produced at the beginning of the electrolysis from the simple and undecomposed guanidonium salt. As the electrolysis proceeds, ammonium ions become more numerous in the liquid and these account for the increasing production of hydrogen at the cathode. At the beginning of the electrolysis there is nothing in the anode compartment which can be oxidized, and the oxygen escapes as gas. Later, cyanide ions accumulate near the anode. The oxidation of these to cyanate ions accounts for the decreasing evolution of oxygen, and the hydrolysis, by the action of the acid solution, of a part of the cyanic acid to ammonia explains the small amount of urea which has been found in the anode compartment.

TABLE I

POTENTIOMETER MEASUREMENTS AT 0° ON THE CELL: AMALGAM/0.1 *N* GUANIDONIUM SULFATE/0.05 *M* H_2SO_4/$HgSO_4$ IN 0.05 *M* H_2SO_4/Hg

Time, min.	Potentiometer readings, v. Expt. 1	Expt. 2	Expt. 3
	Electrolysis going on		
1	2.31	2.70	2.69
2	...	...	2.99
4	...	2.80	...
5	2.09	...	...
6	...	...	2.66
7	...	...	2.33
8	1.91	...	...
9	...	2.26	1.74
11	1.14	1.50	1.30
13	...	1.08	1.08
15	...	0.72	0.88
17	...	.78	.73
19	...	.71	...
	Electrolysis stopped		
1.5	...	...	0.13
2.0	...	0.29	...
3.0	0.30	...	...

Experiments

Only experimental details which are not sufficiently clear from the foregoing discussion are reported here.

The potentiometer readings in the experiments in which the polarization of the respective amalgams in contact with 0.1 *N* solutions of guanidonium sulfate, ammonium sulfate, and potassium sulfate were measured are reported in Tables I, II, and III. In each of the experiments the electrolyzing current was 0.1 ampere (35 to 40 volts).

TABLE II

POTENTIOMETER MEASUREMENTS AT 0° ON THE CELL: AMALGAM/0.1 *N* $(NH_4)_2SO_4$/0.05 *M* H_2SO_4/$HgSO_4$ IN 0.05 *M* H_2SO_4/Hg

Time, min.	Potentiometer readings, v. Expt. 1	Expt. 2
	Electrolysis going on	
1	0.74	0.80
2	.81	.81
3	.82	...
4	.85	...
5	...	.85
6	.88	...
7	.86	.88
9	.96	.98
11	.98	...
14	...	1.00
16	...	1.03
	Electrolysis stopped	
1	1.43	1.59
2	1.46	...
3	1.28	...
4	1.22	...
5	1.42	1.28
8	1.41	...
9	...	1.39
24	1.69	...

Analyses of the gases from the electrolysis of guanidonium carbonate solution (mercury cathode and platinum anode) are reported in Table

TABLE III

POTENTIOMETER MEASUREMENTS AT 0° ON THE CELL: AMALGAM/0.1 *N* K_2SO_4/0.05 *M* H_2SO_4/$HgSO_4$ IN 0.05 *M* H_2SO_4/Hg

Time, min.	Potentiometer readings, v. Expt. 1	Expt. 2
	Electrolysis going on	
1	0.93	0.82
2	.92	...
3	...	.84
4	...	.91
5	.91	...
6	...	.94
8	1.05	...
9	...	.97
14	1.08	...
17	1.09	1.05
	Electrolysis stopped	
3	1.21	1.17
5	1.22	...
7	...	1.18
10	1.29	...
22	1.33	...

IV. The small amount of oxygen in the anode gases may perhaps be explained by supposing that it comes from air dissolved in the electrolyte. The same cause would introduce a small error in the figure for the oxygen of the anode gases. The amount of nitrogen, both in the cathode and in the anode gases, is much greater than could be derived from air dissolved in the electrolyte.

Since ammonium salts are absent at the beginning of the electrolysis, we conclude that ammonia is produced in the electrolyte by the action of the current on the guanidonium salt. The fact that guanidonium salts cannot be reduced by catalytic hydrogenation, or by any other known means, excludes the likelihood that the ammonia results from electrolytic reduction.

When guanidonium carbonate solutions are electrolyzed, oxygen is evolved at the anode much faster at the beginning of the experiment than hydrogen is evolved at the cathode. Later, hydrogen is evolved more abundantly, even three times as rapidly as the oxygen.

The acidic anode liquid contains prussic acid and a small amount of urea. The strongly ammoniacal cathode liquid contains considerable amounts of urea, and no cyanide. Neither contains formic, oxalic, or cyanic acid, biuret, or cyanamide.

The facts are explained by supposing that the guanidonium ion is the triamino-carbonium ion, that this is discharged at the cathode, doubling up (without production of hydrogen) to form the intermediate, unstable hexaaminoethane which breaks down into ammonia and cyanogen: the latter reacts with part of the ammonia to form cyanide and urea. The increasing concentration of ammonia accounts for the increasing evolution of hydrogen as the electrolysis proceeds. The cyanide ions migrate to the anode and are in part oxidized to cyanic acid which by being in part hydrolyzed to ammonia yields urea. Their oxidation accounts for the decreasing evolution of oxygen.

TABLE IV

GASES FROM ELECTROLYSIS OF GUANIDONIUM CARBONATE SOLUTION

Conditions of experiment	20% solution, 0.5 ampere Cathode gases		Anode gases		5% solution, 0.1 ampere Cathode gases			Anode gases		
Removed after, hours	1	2	1	2	3	6	9	3	6	9
Volume, cc.	79.1	91.6	101.4	100.2	95.0	180.6	127.4	73.8	58.4	42.8
Ammonia and amines, %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon dioxide, %	.0	.0	.0	.0	.0	.7	.0	.0	2.1	.0
Unsaturated, %	.6	.0	.0	.0	.4	.0	.0	2.03	0.8	1.9
Oxygen, %	1.4	1.5	93.0	94.4	1.3	.9	.4	90.0	85.0	83.0
Hydrogen, %	88.0	91.2	0.0	0.0	90.3	93.5	88.3	0.0	0.0	0.0
Hydrocarbons, %	0.0	0.0	.0	.0	0.0	0.0	0.0	.0	.0	.0
Nitrogen (residue), %	10.0	7.3	7.0	5.6	8.0	4.9	11.3	8.0	12.1	15.1
Ratio: vol. cathode gases/vol. anode gases			0.78	0.90				1.3	3.1	3.0
Ratio: vol. hydrogen/vol. oxygen			.74	.88				1.3	3.4	3.2

Summary

Polarization measurements at 0° show that the amalgam which is produced when guanidonium salts are electrolyzed with a mercury cathode lasts only two or three minutes after the electrolyzing current is shut off. The electrolysis of guanidonium salts in organic solvents at −30 to −40° yields ammonium amalgam.

CAMBRIDGE, MASS.

RECEIVED AUGUST 7, 1937