It is, indeed, quite unnecessary in conductivity work to invite the troubles involved in the preparation of purer water than the saturated H_2CO_3 solution. The aim should rather be to exclude all other conducting impurities except H_2CO_3, and make for this an *exact* correction. The application of such a correction to electrolytes of different types at very high dilutions will be discussed in a succeeding article.

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[Contribution from the Chemical Laboratory of the University of California.]

THE HYDROLYSIS OF HEXAHYDROPYRIMIDINE.

By Gerald E. K. Branch.

Received August 30, 1916.

Introduction.

The study of the catalytic action of hydrogen ion has been recently extended to many cases in which the hydrogen ion decreases instead of increasing the speed of the reactions. The most notable of these investigations have been carried on by Biddle and his co-workers.

It appears that it is by no means uncommon for hydrogen ion to have a retarding effect. In fact in the case of additions to a nitrogen-carbon linkage, it might be expected from theoretical grounds that H^+ should act as a negative catalyst when there is a tautomeric change involving the nitrogen atom. An example of such a reaction was found by Titherley and Branch[1] in the hydrolysis[2] of hexahydropyrimidine. It was there shown that this substance is tautomeric with methylene-α,γ-diaminopropane and that its hydrolysis to formaldehyde and trimethylenediamine is negatively catalyzed by hydrogen ion. Although they did not study this reaction quantitatively, they suggested that the effect of hydrogen ion was due to its favoring the less readily hydrolyzable ring form, a suggestion which has been verified by the author.

When an allelotropic mixture undergoes a reaction which is slow enough to allow equilibrium to be maintained between the isomers, any change in conditions which affects this equilibrium must have a corresponding influence on the reaction. In cases which involve a tautomeric shift about a nitrogen atom the isomers will show very different tendencies to form ions of the type of ammonium ion. The ability to add by virtue of a change of valence of the nitrogen varies inversely with the ability to add at the carbon nitrogen bond. Thus pyridine is a weaker base than piperidine but stronger than imines, just as benzene shows greater powers of addition than cyclohexane, but less than ethylenes.

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[1] *J. Chem. Soc.*, 103, 330 (1913).

[2] In this paper hydrolysis is assumed to be preceded by an addition. For the argument, however, it is only necessary that it be a reaction which takes place more readily at a double than at a single bond.

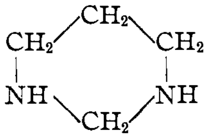
In an allelotropic mixture between the substances HA—CH=NR and A=HC—NHR and their hydrogen ion compounds H—A—CH=N$^+$HR and A=HC—N$^+$H$_2$R, where A and R represent any groups, the following equilibria are established: Ha—CH=NR $\rightleftarrows$ A=HC—NHR, HA—CH=N$^+$HR $\rightleftarrows$ A=HC—N$^+$H$_2$R, HA—CH=NR+H$^+$ $\rightleftarrows$ HA—CH=N$^+$HR, and A=HC—NHR+H$^+$ $\rightleftarrows$ A=HC—N$^+$H$_2$R, and from the laws of equilibrium there will be the following relationships among the concentrations of the substances:

$$\frac{(\mathrm{A{=}HC{-}NHR})}{(\mathrm{HA{-}CH{=}NR})} = k_1, \quad \frac{(\mathrm{A{=}HC{-}N^+H_2R})}{(\mathrm{HA{-}CH{=}N^+HR})} = k_2,$$

$$\frac{(\mathrm{HA{-}CH{=}N^+HR})}{(\mathrm{HA{-}CH{=}NR})x(\mathrm{H^+})} = k_3 \text{ and } \frac{(\mathrm{A{=}HC{-}N^+H_2R})}{(\mathrm{A{=}CH{-}NHR})x(\mathrm{H^+})} = k_4$$

Hence $k_1 = \frac{k_3}{k_4} k_2$, and since it has been shown above that k_4 is greater than k_3, it follows that k_2 is greater than k_1. Since an increase in concentration of hydrogen ion must favor the ionic forms, it decreases the proportion in which the double bond is situated between carbon and nitrogen, and consequently retards any additions taking place at the carbon-nitrogen linkage, insofar as its action is due to its effect on the equilibrium between the tautomers.

In the case of hexahydropyrimidine the tautomerism is between



and CH$_2$ = N.CH$_2$.CH$_2$.CH$_2$.NH$_2$.

Hydrogen ion, according to the rules given above, will greatly favor the former, while only the latter, in virtue of its double bond, will hydrolyze at an appreciable rate. This case is further complicated by the fact that methylene-α,γ-diaminopropane undergoes polymerization.[1] Acid solutions will contain chiefly hexahydropyrimidine as its disalt, but there will also be some monosalt of methylene-α,γ-diaminopropane and its polymers. It is only these latter substances which are directly acted on during hydrolysis, but as they are removed the hexahydropyrimidine reforms them until it also has disappeared. It will be shown later that the rates of the hydrolysis under different conditions of hydrogen ion concentration and temperature agree with this representation of its mechanism.

The Nature of the Relation.

It has been shown by Titherley and Branch that when the hydrochloride of methylene-α,γ-diaminopropane is allowed to stand with an excess of mineral acid, and afterwards titrated with alkali, using methyl orange

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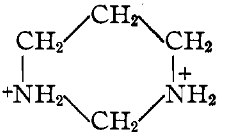
[1] Titherley and Branch, *J. Chem. Soc.*, 103, 332 (1913).

as the indicator, a slow change takes place, which results in the neutralization of an equivalent of acid, and that the rate of the change is an inverse function of the acid concentration.

They suggested two reactions which might account for this phenomenon, namely,

I. $CH_2=N.CH_2.CH_2.CH_2.NH_3^+ + H^+ \rightleftarrows$



and

$$\text{II. } CH_2=N.CH_2.CH_2.CH_2.NH_3^+ + H_2O + H^+ \rightleftarrows$$
$$CH_2O + NH_3^+.CH_2.CH_2.CH_2.NH_3^+;$$

and expressed the opinion that it was due to a combination of these two causes. They obtained evidence that both of these reactions could take place, and positive evidence that the phenomenon was at least in part due to the latter. However, they obtained no evidence that the former was not an almost immediate reaction, and hence could not account for the slow neutralization, and owing to its reversal its effect could not be observed by the above experiment.

That this reaction is, in fact, too fast to account for a slow change is shown by the following experiment. A solution of the hydrochloride of methylene-α,γ-diaminopropane was added to a solution containing methylviolet and enough hydrochloric acid to give a green color. The color immediately changed to a blue, corresponding to the neutralization of an amount of acid equivalent to the hydrochloride added, according to Equation I.

There was no noticeable further change of color after standing for more than an hour.

Experimental Method.

Solutions of trimethylene diamine, formaldehyde, and hydrochloric acid were mixed in equimolecular proportions. The resulting mixture is chiefly a solution of the hydrochloride of methylene-α,γ-diaminopropane, in equilibrium with small quantities of CH_2O and $NH_2.CH_2.CH_2.CH_2.NH_2$, HCl, and also some other products of the union of the two latter substances.

Measured volumes of this solution and standardized HCl were mixed and immersed in a thermostat. After an interval of from five to ten minutes[1] 20 cc. portions were withdrawn, from time to time, run into a mixture of ice and salt, and titrated, as rapidly as possible, with a 0.1 *N* solution of NaOH, using methyl orange as the indicator.

A peculiar phenomenon was observed during this titration. The solu-

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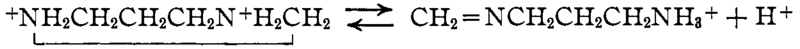
[1] Rough estimates of the methylene-α,γ-diaminopropane in the original solution, made by calculating the amount hydrolyzed in this interval, give about 90% of a quantitative yield.

tion just becomes yellow, then changes back to pink; on further standing the solution again becomes yellow, even (although more slowly) when the solution is kept in a freezing mixture.

There are four possible explanations. Firstly, the reaction



$$^{+}NH_2CH_2CH_2CH_2N^{+}H_2CH_2 \rightleftarrows CH_2{=}NCH_2CH_2CH_2NH_3^{+} + H^{+}$$

may be slow enough at this temperature, —5° to —10° to be noticeable. Secondly, the hydrolysis of $NH_3^{+}.CH_2.CH_2.CH_2.NH_3^{+}$ may be slow. Thirdly,[1] CH_2O may form a compound with H^{+} which decomposes at a noticeable rate. Fourthly, CH_2O may have combined with $NH_2.CH_2.CH_2.CH_2.NH_2$ in the original condensation to form traces of compounds more readily hydrolyzable than $CH_2{=}N.CH_2.CH_2.CH_2.NH_2$. If this were the case, during hydrolysis these substances would be reduced to concentrations which are no longer in equilibrium with the $CH_2{=}N.CH_2.CH_2.CH_2.NH_2$ in a neutral solution, and must reform, on neutralization, by the union of CH_2O with $NH_3^{+}.CH_2.CH_2.CH_2.NH_3^{+}$ or $CH_2{=}N{-}CH_2.CH_2.CH_2.NH_3^{+}$, to give H^{+}. Further hydrolysis would then take place, reducing the H^{+} concentration, until a state of equilibrium is reached.

The first explanation is untenable, as the formation of acid becomes more marked as the hexahydropyrimidine is used up by hydrolysis. The second and third explanations can be shown to be unsound by the fact that neither solutions of CH_2O nor of $NH_2.CH_2.CH_2.CH_2.NH_2$, when allowed to stand with excess of HCl and rapidly neutralized in the presence of ice and salt, become acid to methyl orange on standing. The last hypothesis is the only one which agrees with all the facts observed. In solutions in which all the hexahydropyrimidine has been hydrolyzed the acid formed after neutralization is permanent, also when solutions of CH_2O and $^{+}H_3N.CH_2.CH_2.CH_2.NH_3^{+}$ are mixed, there is a gradual formation of a small amount of H^{+}, which is permanent. In these cases the H^{+} is probably chiefly produced by the reaction $CH_2O + {}^{+}H_3N.CH_2.CH_2.CH_2.NH_3^{+} \rightleftarrows CH_2{=}N.CH_2.CH_2.CH_2.NH_3^{+} + H^{+}$.

For these reasons the first appearance of yellow was taken as the end point, and the titration was performed as rapidly as possible, and the solution vigorously agitated during the process. Naturally, accurate determinations cannot be made under these circumstances, but the measurements made after the reaction had been allowed to go to completion gave results within 5% of the theoretical amount of total amine.

The results at 25° are given in Table I. The first column gives the times from the first titration. The second column gives the concentration of acid as given by the titration. The last figure in this column gives the actual excess of acid above that necessary to form

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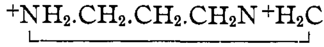
[1] This explanation was suggested to the author by Dr. E. Q. Adams.



$^{+}NH_2.CH_2.CH_2.CH_2N^{+}H_2CH_2$ or $^{+}H_3N.CH_2.CH_2.CH_2.NH_3^{+}$.

The third column gives the concentration of hexahydropyrimidine, and is obtained by subtracting the final from the actual acid titer. The significance of the fourth column will be discussed later. All concentrations are expressed in mols per liter.

TABLE I.—EXPERIMENTAL RESULTS AT 25° ± 0.02°.

Time in minutes.	Conc. of acid by titration.	Conc. of $CH_2{=}N.CH_2.CH_2.CH_2.NH_2$.	$K_2 \times 10^3$.
	Experiment 1.		
0	0.1282	0.0291	..
4.92	0.1254	0.0263	3.32
13.75	0.1208	0.0217	3.59
28.75	0.1158	0.0167	3.46
∞	0.0991	0	..
			Mean, 3.46
	Experiment 2.		
0	0.0768	0.0140	..
12.67	0.07195	0.00915	3.66
32.58	0.06875	0.00595	3.43
∞	0.0628	0	..
			Mean, 3.55
	Experiment 3.		
0	0.2031	0.0613	..
6.33	0.1967	0.0549	3.32
18.17	0.1854	0.0436	3.82
31.67	0.1760	0.0342	3.98
∞	0.1418	0	..
			Mean, 3.71
	Experiment 4.		
0	0.2505	0.0631	..
8.33	0.2440	0.0566	3.89
20.42	0.2360	0.0486	3.87
54.33	0.2210	0.0336	3.78
∞	0.1874	0	..
			Mean, 3.85
	Experiment 5.		
0	0.3474	0.0482	..
24.83	0.3396	0.0404	4.40
78.75	0.3301	0.0309	3.64
∞	0.2992	0	..
			Mean, 4.02
	Experiment 6.		
0	0.2699	0.0769	..
12.25	0.2595	0.0665	3.27
26.83	0.2481	0.0551	3.57
59.58	0.2316	0.0386	3.62
∞	0.1930	0	..
			Mean, 3.49
	Experiment 7.		
0	0.1420	0.0402	..
6.92	0.1349	0.0331	3.92
26.00	0.1241	0.0223	3.69
49.33	0.1165	0.0147	3.62
∞	0.1018	0	..
			Mean, 3.74

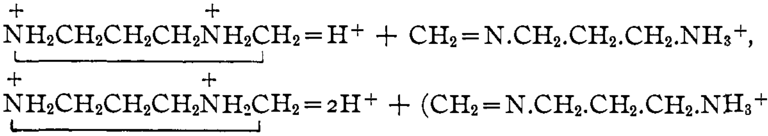
Discussion of Results.

According to the mechanism suggested in this paper for the hydrolysis of hexahydropyrimidine, the rate of the reaction should depend on the concentrations of the various derivatives of its open chain tautomer, and should be given by the equation

$$\frac{dx}{dt} = k_{r_1}y_1 + k_{r_2}y_2 + k_{r_3}y_3 + , \dots\dots \tag{1}$$

where x represents the concentration of trimethylene diamine formed, and y_1, y_2, etc., represent the concentrations of the derivatives of methylene-α,γ-diaminopropane.

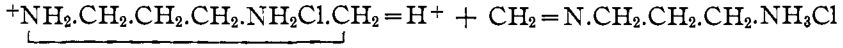
In dilute solutions, these substances will be present chiefly as their ions, which will be in equilibrium with the ion of hexahydropyrimidine according to the equations



$$\underline{\overset{+}{N}H_2CH_2CH_2CH_2\overset{+}{N}H_2CH_2} = H^+ + CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+,$$

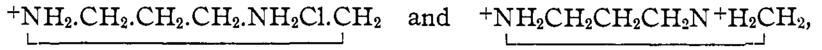
$$\underline{\overset{+}{N}H_2CH_2CH_2CH_2\overset{+}{N}H_2CH_2} = 2H^+ + (CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+)_2,$$

etc. Such an equilibrium as



$$\underline{{}^+NH_2.CH_2.CH_2.CH_2.NH_2Cl.CH_2} = H^+ + CH_2{=}N.CH_2.CH_2.CH_2.NH_3Cl$$

may well be neglected, not only on account of the dilute nature of the solution, but also because owing to the similarity of



$$\underline{{}^+NH_2.CH_2.CH_2.CH_2.NH_2Cl.CH_2} \quad \text{and} \quad \underline{{}^+NH_2CH_2CH_2CH_2N^+H_2CH_2},$$

and of

$$CH_2{=}N.CH_2.CH_2.CH_2.NH_3Cl \text{ and } CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+,$$

such an equilibrium will be very similar to the corresponding equilibrium involving the fully ionized forms, and the rates of hydrolysis of

$$CH_2{=}N.CH_2.CH_2.CH_2.NH_3Cl$$

practically the same as that of

$$CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+.$$

According to the laws of equilibrium, the concentrations of the various substances present will be related by the equations

$$\frac{y_1(H^+)}{a} = k_{e_1}, \quad \frac{y_2(H^+)^2}{a^2} = k_{e_2}, \text{ etc.,} \tag{2}$$

where y_1 is the concentration of $CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+$, y_2 the concentration of $(CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+)_2$, and a the concentration of $\underline{{}^+NH_2CH_2CH_2CH_2N^+H_2CH_2}$.

Since in solutions whose concentrations of H^+ are of the same order of magnitude as in those actually used there is but little diminution of H^+ during the reaction, we have the following approximate relationships: $a = (c_1 - x)\alpha_1$, and $(H^+) = c_2\alpha_2$, where c_1 is the initial concentration of hexahydropyrimidine in all its forms, α_1 the degree of ionization of its dihydrochloride, c_2 the final concentration of HCl, and α_2 the degree of ionization of the HCl. Substituting in Equations 2 we get

$$\frac{y_1c_2\alpha_2}{(c_1-x)\alpha_1} = k_{e_1}, \quad \frac{y_2(c_2\alpha_2)^2}{\{(c_1-x)\alpha_1\}^2} = k_{e_2}, \text{ etc.}$$

For dilute solutions the approximate forms

$$\frac{y_1 c_2}{c_1 - x} = k_{e_1}, \quad \frac{y_2 c_2^2}{(c_1 - x)^2} = k_{e_2}, \text{ etc.,} \tag{3}$$

will introduce errors no greater than experimental. By combining Equations 1 and 3 we get the relationship

$$\frac{dx}{dt} = \mathrm{K}_1 \frac{c - x}{c_2} + \mathrm{K}_2 \frac{(c-x)^2}{c_2} + \ldots\ldots \tag{4}$$

Neglecting all but the first two terms on the right-hand side of this equation (which corresponds to neglecting all polymers of methylene-α,γ-diaminopropane higher than dimolecular) and integrating gives

$$\frac{c_2}{\mathrm{K}_1/\mathrm{K}_2\, t} \log \frac{c_1(c_1 - x + c_2\, \mathrm{K}_1/\mathrm{K}_2)}{(c_1 - x)(c_1 + c_2\, \mathrm{K}_1/\mathrm{K}_2)} = \mathrm{K}_2.$$

The experimental results, substituted into this equation, give values for K_2 constant within experimental error, for all values of $\mathrm{K}_1/\mathrm{K}_2$ between $^1/_2$ and $^1/_4$. K_2 has therefore been calculated in this paper by assuming $\mathrm{K}_1/\mathrm{K}_2 = {}^1/_3$.

The results at 25° have been collected in Table II, in which the first value obtained in each experiment has been neglected, except in the case of Experiment 2.

Table II.—$\mathrm{K}_1/\mathrm{K}_2 = {}^1/_3$. Temperature = 25°.

No. of Expt.	c_1.	$c_1 - x$.	c_2.	$\mathrm{K}_2 \times 10^3$.
1	0.0291	0.0217	0.0991	3.59
1	0.0291	0.0167	0.0991	3.46
2	0.0140	0.00915	0.0628	3.66
2	0.0140	0.00595	0.0628	3.43
3	0.0613	0.0436	0.1418	3.82
3	0.0613	0.0342	0.1418	3.98
4	0.0631	0.0486	0.1874	3.87
4	0.0631	0.0336	0.1874	3.78
5	0.0482	0.0309	0.2992	3.64
6	0.0769	0.0551	0.1930	3.57
6	0.0769	0.0386	0.1930	3.62
7	0.0402	0.0223	0.1018	3.69
7	0.0402	0.0147	0.1018	3.62
				Mean, 3.67

The Effect of Change of Temperature.

A study of the effect of the change of temperature on the rate of the reaction gives further corroboration of the mechanism suggested for the hydrolysis of hexahydropyrimidine. According to this theory, change of temperature should have an abnormally large effect on the rate, for not only will there be the usual increase of reaction rate with temperature, but there will be an increase in the concentrations of the substances actually undergoing hydrolysis, for the reactions

$$\mathrm{CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+ + H^+ = {}^+\underline{NH_2.CH_2.CH_2.CH_2.N^+H_2.CH_2}}$$

and

$$\mathrm{(CH_2{=}N.CH_2.CH_2.CH_2.NH_3^+)_2 + 2H^+ = {}^+\underline{NH_2.CH_2.CH_2.CH_2.N^+H_2.CH_2}},$$

since they involve neutralization, are presumably exothermic. Also, since the heat of the latter reaction is probably the greater, it might be expected that the ratio K_1/K_2 will decrease with rise of temperature. Unfortunately, this latter point cannot be decided from the data given in this paper, as the value K_1/K_2 has not been obtained with sufficient accuracy. It has been shown, however, that the reaction has a high temperature coefficient. The mean value of K_2 was found to be 3.67×10^{-3} at 25° and 1.46×10^{-3} at 18.4°, when K_1/K_2 is assumed to be equal in both cases.

The results obtained at 18.4° are given in Tables III.

Table III.—$K_1/K_2 = {}^1/_3$. Temperature = 18.4° ± 0.02°.

Time in minutes.	Conc. of acid titration.	Conc. of $\mathrm{CH_2{=}N.CH_2.CH_2.CH_2.NH_2}$.	$K_2 \times 10^3$.
	Experiment 8.		
0	0.2065	0.0522	..
43.2	0.1948	0.0405	1.44
90.0	0.1876	0.0333	1.28
135.5	0.1812	0.0269	1.31
∞	0.1543	0.0	..
		Mean,	1.34
	Experiment 9.		
0	0.1613	0.0255	..
60.75	0.1545	0.0187	1.42
117.8	0.1496	0.0138	1.50
	Experiment 9 (*continued*).		
187.3	0.1455	0.0097	1.55
∞	0.1358	0.0	..
		Mean,	1.49
	Experiment 10.		
0	0.2427	0.0494	..
163.5	0.2185	0.0252	1.54
231.0	0.2132	0.0199	1.53
∞	0.1933	0.0	..
		Mean,	1.54

The Effect of Alcohol and of Sodium Chloride.

Alcohol was found to accelerate the rate of this reaction. Dr. Lewis suggested to me that if alcohol, which is less electrophyllic than water, increased the rate, the addition of sodium chloride would probably have the reverse effect. This surmise proved to be correct when the concentrations of salt were high. However, low concentrations of salt increase the rate of hydrolysis. The results of one experiment in the presence of alcohol and four experiments in varying concentrations of sodium chloride are given in Table IV. In each case K_2 has been calculated by the equation used in the previous experiments, and the same value for K_1/K_2 assumed.

TABLE IV.—$K_1/K_2 \doteq {}^1/_3$. Temperature = 25°.

Time in minutes.	Conc. of acids by titration.	Conc. of $CH_2=N.CH_2.$-$CH_2.CH_2.NH_2$.	$K_2 \times 10^3$.
Experiment 11.	$C_2H_5.OH$ = 6.81 M.		
0	0.2215	0.0223	..
17.6	0.2113	0.0121	15.8
39.9	0.2065	0.0073	13.2
∞	0.1992	0.0	..
			Mean, 14.5
Experiment 12.	NaCl = 0.0573 M.		
0	0.2206	0.0279	..
10.9	0.2164	0.0237	6.17
32.4	0.2106	0.0179	5.87
71.8	0.2043	0.0116	5.50
	0.1927	0.0	..
			Mean, 5.85

Time in minutes.	Conc. of acids by titration.	Conc. of $CH_2=N.CH_2.$-$CH_2.CH_2.NH_2$.	$K_2 \times 10^3$.
Experiment 13.	NaCl = 0.1039 M.		
0	0.2222	0.0276	..
24.25	0.2145	0.0199	5.78
46.7	0.2100	0.0154	5.53
∞	0.1946	0.0	..
			Mean, 5.66
Experiment 14.	NaCl = 0.173 M.		
0	0.2223	0.0278	..
22.9	0.2153	0.0208	5.39
45.75	0.2119	0.0174	4.49
∞	0.1945	0.0	..
			Mean, 4.94
Experiment 15.	NaCl = 1.614 M.		
0	0.2185	0.0322	..
27.3	0.2136	0.0273	2.29
53.6	0.2107	0.0244	1.99
∞	0.1863	0.0	..
			Mean, 2.14

Summary.

The effect of hydrogen ion on addition reactions of any allelotropic mixture, involving a tautomeric shift about a nitrogen atom, is discussed. It is pointed out that in such cases hydrogen ion may be expected to act as a negative catalyst.

The rate of hydrolysis of hexahydropyrimidine was measured under varying concentrations of hydrogen ion, and at two temperatures. Both the effect of hydrogen ion and of temperature on the rate of this reaction were found to be in agreement with this theory.

Alcohol was found to increase the rate of hydrolysis of hexahydropyrimidine.

Sodium chloride in low concentrations was found to increase the rate of this reaction, while in higher concentrations it acts as a negative catalyst.

BERKELEY, CAL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE SILVER SALT OF TRIIODOPHENOL AND ITS CATALYTIC DECOMPOSITIONS.

BY G. H. WOOLLETT.

Received August 21, 1916.

In the course of further study of the catalytic decomposition of silver salts described by Hunter,[1] *et al.*, it became necessary to investigate the

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[1] THIS JOURNAL, 38, 1761 (1916).