

pheric oxygen. With the hydrogen peroxide, however, they are comparatively ineffective.

### Summary

1. Hydrogen peroxide in the presence of ferric salts (Fenton's reagent) oxidizes ethanol to acetic acid. The reaction is quantitative. This reaction is paralleled by the catalytic decomposition of the hydrogen peroxide by the ferric ions. The two reactions are approximately unimolecular.

2. Acids retard the speed of these reactions. In solutions of equivalent concentrations the order of increasing effectiveness is acetic, nitric, hydrochloric, sulfuric.

3. The speed of the two reactions is directly proportional to the concentration of the catalyst.

4. The reaction velocity increases with the concentration of the hydrogen peroxide.

5. Ferrous salts have been shown to be just as effective as ferric salts, inasmuch as they are immediately oxidized to the trivalent condition.

6. Evidence has been obtained that the ethanol is oxidized through the formation of ferric acid as an intermediate.

7. The oxidation of the ethanol to acetic acid is followed by the oxidation of the acetic acid to carbon dioxide and water.

8. Other salts substituted for the ferric compounds in Fenton's reagent have been found to be unsatisfactory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

## CATALYSIS IN BUFFER SOLUTIONS. I

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The general purpose of this work was to study the velocity of various reactions in small concentrations of hydrogen and hydroxyl ions. The study necessitated the use of buffer solutions and a consideration of the effect of neutral salts. A preliminary study indicated that with certain limitations several reactions are suitable for the purpose: (1) the decomposition of nitrosotriacetoneamine; (2) the decomposition of diazoacetic ester; (3) the reaction between acetone and iodine as catalyzed by hydrogen ion; (4) the mutarotation of sugars; (5) the hydrolysis of the esters. The last two reactions are catalyzed by both hydrogen and hydroxyl ions and permit a study of the catalytic minimum point.

The present paper deals with the decomposition of nitrosotriacetoneamine, catalyzed by hydroxyl ions. The reaction has been studied by

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Francis<sup>2</sup> and his students, and more recently by Brönsted<sup>3</sup> and King. Francis found the reaction to be complicated at concentrations of hydroxyl ion above 0.05 *N*. With small concentrations of hydroxyl ion the reaction appears to be a simple decomposition catalyzed by hydroxyl ion. Francis' results indicated that below 0.2 *N* total equivalent salt concentration the salt effect would be negligible for the work contemplated. The recent results of Brönsted and King show a salt effect for 0.01 *N* sodium hydroxide solution at 15° amounting to 7% in 0.1 *N* salt solution. The suggestion was made that this higher salt effect might be due to the lower concentrations and temperature. In order to clear up these apparent discrepancies, and to determine the temperature coefficient more accurately, the study of the reaction velocity in dilute solutions of sodium hydroxide was continued before the study in buffer solutions was undertaken.

The rate of reaction can be followed conveniently by measuring the volume or the pressure of the gas evolved. The pressure method is not readily applicable to high temperatures and consequently the volume method was adopted. In either case the most important point is "to agitate the solution to such an extent that the gas is registered on the volume- (or pressure-) measuring apparatus as soon as it is formed in the solution."<sup>4</sup> The importance of this factor has been emphasized by recent work on supersaturation.<sup>5</sup>

### Experimental Method

Florence flasks were fitted with rubber stoppers through which passed mercury-sealed stirrers with outlets attached; the stirrers were a modified form of that described by Reid.<sup>6</sup> The shaft was fitted with a detachable glass stirrer of the Witt type with two extra prongs to break the surface of the liquid. For work up to 40° the temperature was controlled within 0.01° by two electrically regulated thermostats. The differences in temperature between the reacting solutions and the baths, due to stirring, were avoided in the long-time experiments by shutting off the stirrers between readings. For the work at 60° and at 80° double-walled vapor-baths of chloroform and of benzene were used as thermostats.

To carry out an experiment, the solution of the buffer mixture or base was siphoned into the reaction vessel which was stoppered and placed in the thermostat. When the solution had come to temperature a weighed amount of the nitrosotriacetoneamine was added, the stirrer inserted, and

<sup>2</sup> Francis and Clibbens, *J. Chem. Soc.*, **101**, 2358 (1912). Francis and Geake, *ibid.*, **103**, 1722 (1913). Francis, Geake and Roche, *ibid.*, **107**, 1651 (1915).

<sup>3</sup> Brönsted and King, *THIS JOURNAL*, **47**, 2523 (1925).

<sup>4</sup> Harned, *ibid.*, **40**, 1464 (1918).

<sup>5</sup> Findlay and students, *J. Chem. Soc.*, **103**, 1170 (1913); **105**, 1297 (1914); **121**, 1046 (1922). Metschl, *J. Phys. Chem.*, **28**, 417 (1924).

<sup>6</sup> Reid, *THIS JOURNAL*, **37**, 2112 (1915).

the outlet connected to the gas buret. After the stirrer had thoroughly mixed the solution, and 1 or 2 cc. of gas had been given off, the buret reading and the time were taken. Readings were taken at suitable intervals and the reaction was allowed to run to completion when the final reading was made. In the preliminary experiments it was found necessary to exclude oxygen as well as carbon dioxide, so all experiments were run in an atmosphere of nitrogen.

The velocity constants were calculated by the equation  $k = (2.30/t) \cdot (\log v_\infty - v_0/v_\infty - v_t)$ , where  $v_\infty$  is the final reading,  $v_0$  the initial and  $v_t$  the reading at time  $t$ .

Preliminary experiments showed that stirring above 1500 r.p.m. gave reproducible results which were unaltered at speeds as high as 4000 r.p.m.

Table I gives the results of a series of experiments at 30° for various concentrations of reactants. The last column is included for the sake of comparison with the data of Francis. His  $k/[\text{OH}^-]$  value, calculated in the same way, was 1.92.

TABLE I  
DECOMPOSITION OF NITROSOTRIACETONEAMINE IN NaOH SOLUTIONS

R.p.m.	Approx. molarity nitroso-amine	Normality NaOH	$k$	$k/[\text{NaOH}]$	$k/[\text{OH}^-]$
1500	0.006	0.006190	0.0115	1.86	1.91
2000	.017	.006190	.0116	1.87	1.92
3000	.006	.005420	.01005	1.85	1.90
1500	.006	.005420	.00957	1.77	1.81
4000	.022	.01542	.0274	1.78	1.85
1500	.022	.01542	.0273	1.77	1.84
4000	.015	.01000	.0182	1.82	1.89
2000	.015	.02250	.0397	1.77	1.86
4000	.015	.02250	.0414	1.84	1.94
2000	.015	.01110	.0202	1.82	1.89
1500	.015	.002585	.00493	1.91	1.95
3000	.015	.002585	.00500	1.93	1.97
3000	.015	.01760	.0313	1.78	1.87
					Av. 1.89
					a. d., 2%

To check the work of Brönsted and King the velocity was determined at 15° with 0.0100 *N* sodium hydroxide solution and  $k$  was found to be 0.00442. Multiplying Brönsted and King's velocity constant by 2.30 one obtains 0.00437. From this it is evident that the experimental method gives results in fair agreement with the results of the authors mentioned.

### The Temperature Coefficient

The rate of reaction with 0.01 *N* sodium hydroxide solution at 80° is too rapid for accurate measurement. In order to obtain an accurate value of the temperature coefficient over the range 20–80°, and to eliminate the

error in the standardization of the less concentrated sodium hydroxide solutions, a modification of the "two-thermostat" method<sup>7</sup> was used. A carbonate-free solution of sodium hydroxide was siphoned into four flasks, two of which were placed in each bath. When the solutions had reached the temperatures of the baths, equal weights of nitrosotriacetone-amine were added and the reaction was followed in the usual way. By this means the solutions were made strictly comparable.

Table II gives the temperature coefficients and the corresponding values of  $Q$  from the Arrhenius equation,  $d \ln k/dt = Q/RT^2$ . From the average value of  $Q$ , 16,400, the velocities are calculated for the various temperatures by taking the values of the constant  $k$  at 30° from Table I. The observed values are given for comparison.

TABLE II  
TEMPERATURE COEFFICIENTS

Temp. coeff.	$Q$	$k_{\text{obs. for}}0.0100 \text{ NaOH}$	$T, ^\circ\text{C.}$	$k_{\text{calcd.}}$
$k_{30}/k_{20} = 2.57$	16,700	0.00442	15	0.00441
$k_{40}/k_{30} = 2.42$	16,700	.00708	20	.00717
		.0182	30	....
$k_{60}/k_{40} = 4.75$	16,100	.0440	40	.0436
		$k_{\text{obs. for}}0.00200 \text{ NaOH}$		
		0.00384	30	.....
$k_{80}/k_{60} = 4.02$	16,200	.0441	60	.0452
		.175	80	.184

### Discussion and Study of "Primary Salt Effect"

According to Brönsted's theory<sup>8</sup> a reaction like the decomposition of nitrosotriacetoneamine comes under the general case  $A^\circ$  (non-electrolyte) +  $\text{OH} \rightarrow A(\text{OH})^-$  (the critical complex), where the velocity of the reaction is expressed by the equation  $v = k[A^\circ][\text{OH}^-]f_{A^\circ}f_{\text{OH}^-}/f_{A(\text{OH})^-}$ . Since the activity coefficients are dependent on the ionic type,  $f_0 f_1/f_1$  becomes  $f_0$  and we have<sup>9</sup>  $v = k[A^\circ][\text{OH}^-]f_0$ . Brönsted calls the change in  $f_0$  upon addition of salt "primary salt effect." Generally speaking,  $f_0$  increases from 2 to 4% when the total salt concentration increases from 0.02  $N$  to 0.1  $N$ . The effect is linear. For this particular reaction Brönsted finds  $100k = 0.192 - 0.13c$ , where  $c$  is the total equivalent salt concentration. From this the effect amounts to about 7% in 0.1  $N$  salt solution.

Two questions seem to be worth considering: (1) is the magnitude of the primary salt effect the same when the concentrations of the nitroso-

<sup>7</sup> Rice and Kilpatrick, *THIS JOURNAL*, **45**, 1409 (1923).

<sup>8</sup> (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922). (b) Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924).

<sup>9</sup> More recently Brönsted has introduced an additional term depending on the medium [*Z. physik. Chem.*, **115**, 337 (1925)].

amine and salt are kept constant and the hydroxyl-ion concentration is altered? (2) for identical concentrations of reactants is the magnitude of the salt effect the same at two temperatures?

A method of testing the effect of temperature on primary salt effect at once suggested itself. If the primary salt effect is appreciably different at different temperatures, the temperature coefficient of the reaction should change with addition of salt. This has already been tested in the case of hydrogen-ion catalysis by Rice and Lemkin.<sup>10</sup> They found that although the addition of neutral salt increased the velocity as much as 50%, there was no alteration in the temperature coefficient for the reaction between acetone and iodine, catalyzed by strong monobasic acids. It is true that their temperature range was small, but the accuracy of the method enabled detection of very small differences. No work of this kind has been done for hydroxyl-ion catalysis, and although the nitroso-amine reaction does not lend itself to such a careful study it was thought worth while to carry out some experiments along this line.

The method used was essentially the "two-thermostat" method, all solutions being strictly comparable. The results of a number of experiments are shown in Table III.

TABLE III  
EFFECT OF SALT ON TEMPERATURE COEFFICIENT

Approx. concn. nitroso-amine, <i>M</i>	NaOH, <i>N</i>	NaCl, <i>N</i>	Total equiv. salt concn.	$k_{40}/k_{30}$
0.012	0.01	0.09	0.10	2.38
.012	.01	.09	.10	2.39
.008	.01	.40	.41	2.41
.006	.01	1.00	1.01	2.41
With 0.01 <i>N</i> NaOH alone, the average value of $k_{40}/k_{30}$ is				2.42

Experiments were also carried out at 60° and 80°. The average value of  $k_{80}/k_{60}$  was 4.02 for 0.002 *N* sodium hydroxide solution, while the value in the presence of salt was 4.12. Here the results were not as reproducible as with 0.01 *N* sodium hydroxide at lower temperatures. From the results it is evident that increase in salt concentration causes no appreciable change in the temperature coefficient. Therefore, either the activities of the non-electrolyte and salt change very little with temperature, or there is a compensating effect.

TABLE IV  
REACTION IN GLYCEROL SOLUTION  
0.01 *N* NaOH was used in all experiments

Glycerol, %	$k_{40}$	$k_{20}$	$k_{40}/k_{20}$
0	0.0439	0.0182	2.42
40	.00736	.00294	2.50
40	.00714	.00284	2.51

<sup>10</sup> Rice and Lemkin, *THIS JOURNAL*, **45**, 1896 (1923).

In a previous study of hydrogen-ion catalysis it was found that non-electrolytes do not affect the temperature coefficient in the reaction between acetone and iodine. A few experiments with nitrosotriacetoneamine were carried out in 40% glycerol solution, and the results are recorded in Table IV.

The velocity constants show a decrease of over 80% while the  $k_{40}/k_{30}$  remains practically unchanged. In this connection it is interesting to note the results obtained by Corvin<sup>11</sup> on the change in activity of the hydroxyl ion with increasing concentration of glycerol. At 25° for 0.01 *N* sodium hydroxide solution Corvin gives 0.00883 as the activity of the hydroxyl ion, and for 0.01 *N* sodium hydroxide solution in 40% glycerol he gives the value 0.00135. The activities of the hydrogen ion are  $1.16 \times 10^{-12}$  and  $7.06 \times 10^{-12}$ , respectively. It would appear that the decrease in the velocity of reaction is of the same order as the decrease in the activity of the catalyst. These values also explain why the addition of glycerol increases the rate of reaction for cases of hydrogen-ion catalysis and decreases it for cases of hydroxyl-ion catalysis.

The effect of sodium chloride on the rate of reaction has been determined for 0.01 *N* sodium hydroxide solution at 30° and 40°, and for 0.00190 *N* sodium hydroxide at 60° and 80°. These results can most readily be expressed for dilute solution (up to 0.25 *N*) by the equations below. For the work at 30° and 40° the concentration of the nitrosotriacetoneamine was 0.008 *M*, and at 60° and 80° approximately 0.020 *M*. These concentrations were chosen as being convenient for the experiments in buffer solutions and are approximately those used throughout the rest of the work.

0.0100 <i>N</i> NaOH at 30°	$k = 0.0183 - 0.010c$
at 40°	$k = .0443 - .024c$
0.00190 <i>N</i> NaOH at 60°	$k = .0419 - .024c$
at 80°	$k = .166 - .07c$

In answer to Question 1, previously raised, it might be stated that, in general, for the same total salt concentration the salt effect is greater the lower the concentration of the hydroxyl ion. This would explain the difference in the magnitude of the salt effect between my results and those of Francis. Most of his work was done with higher concentrations of alkali. Below 0.002 *N* sodium hydroxide solution the differences are not detectable, being within the experimental error of the measurements.

### “Secondary Kinetic Salt Effect”

This is discussed in detail by Brönsted<sup>3,3b</sup> and a brief review will suffice here. The secondary kinetic salt effect is ascribed to a change in the concentration of one of the reactants upon the shifting of an equilibrium which involves weak electrolytes. For example, if the hydroxyl ion is in equi-

<sup>11</sup> Corvin, *J. Chem. Soc.*, **127**, 2788 (1925).

librium with a weak base, a change in the salt concentration may markedly alter the concentration of the hydroxyl ion and consequently change the reaction rate. The magnitude and direction of the effect depend on the ionic type involved. In the general case, for ideal solutions, where  $A + B \rightleftharpoons C + OH^-$ , the direction of the change in the concentration of the hydroxyl ion with increase in salt concentration depends on whether the sum of the squares of the ionic charges on A and B is greater or less than the sum of the squares of the charges on C and the hydroxyl ion. If greater, the concentration of the hydroxyl ion is decreased; if less, increased. My results with phosphate buffer at 30° and 40° are in agreement with the work of Brönsted at 15° and will not be given here. However, a few of the results at 80° are given. The buffer solution used was 0.05 *M* in potassium dihydrogen phosphate and 0.0468 *M* in sodium hydroxide. Its Sørensen (*P<sub>H</sub>*) value at room temperature was approximately eight. The equilibrium can be expressed by the equation  $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$  and  $K_a$  (thermodynamic mass-action constant) =  $a_{H_2PO_4^-} a_{OH^-} / a_{HPO_4^{2-}} = [H_2PO_4^-][OH^-] / [HPO_4^{2-}] \cdot f_1^2 / f_2$ , where  $f_1$  and  $f_2$  are the activity coefficients. Now the value of the fraction  $f_1^2 / f_2$  increases with increasing salt concentration. Consequently, the concentration of the hydroxyl ion decreases. The concentration of the hydroxyl ion can be determined by dividing the velocity constant for the buffer solution by the appropriate velocity constant for the nearest sodium hydroxide concentration and the same salt concentration. The nearest sodium hydroxide concentration is 0.001 and the velocity constant can be calculated from the equation  $k = 0.875 - 0.035c$ . From the composition of the buffer solution the concentrations of the other ions are readily obtainable and from them the customary mass-action equilibrium constant,  $K_c$ , can be calculated. Table V gives the results of the calculation.

TABLE V

## DECOMPOSITION OF NITROSOTRIACETONEAMINE IN PHOSPHATE BUFFER SOLUTIONS

KCl	Total equiv. salt concn.	<i>k</i> for buffer	<i>k</i> for 0.001 <i>N</i> NaOH + salt	OH <sup>-</sup> × 10 <sup>5</sup>	<i>K<sub>c</sub></i> × 10 <sup>-6</sup>
0	0.147	0.00280	0.824	3.40	2.33
0	.147	.00282	.824	3.42	2.34
0.031	.178	.00271	.813	3.33	2.28
.067	.214	.00249	.800	3.11	2.13
0	.147	.00281	.824	3.41	2.33
0	.147	.00280	.824	3.40	2.33

$K_c$  decreases with increasing salt concentration. The assumption is made that the magnitude of the primary salt effect is the same for 0.00001 *N* hydroxyl ion as for 0.001 *N*. In his calculations for a different phosphate buffer, Brönsted assumed that the primary salt effect was the same for 0.005 *N* as for 0.01 *N*.

A more rigorous test of the concept of secondary kinetic salt effect was

made in glycine-sodium hydroxide mixtures. Here we have  $\text{NH}_2\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2\text{CH}_2\text{COOH} + \text{OH}^-$ ;  $K_a = [\text{NH}_2\text{CH}_2\text{COOH}][\text{OH}^-]/[\text{NH}_2\text{CH}_2\text{COO}^-]$ .  $f_0 f_1/f_1 = K_c f_0$ . Since the change in  $f_0$  is small for small changes in salt concentration, only a small change in the velocity constant would be expected. Experiments were carried out in which the total equivalent salt concentration was changed from 0.05 *N* to 0.5 *N*. The primary salt effect was determined experimentally for 0.5 *N* total salt concentration. The results obtained with a solution 0.05 *N* in glycine and 0.05 *N* in sodium hydroxide are given in Table VI.

TABLE VI

## DECOMPOSITION OF NITROSOTRIACETONEAMINE IN GLYCINE BUFFER SOLUTIONS

<i>T</i> , °C.	NaCl	Total equiv. salt concn.	<i>k</i> for buffer	<i>k</i> for 0.01 <i>N</i> NaOH + salt	OH <sup>-</sup> concn.	<i>K<sub>c</sub></i> × 10 <sup>-4</sup>
30	0	0.05	0.00342	0.0178	0.00192	0.749
30	0.45	.50	.00357	.0150	.00238	1.19
40	0	.05	.00826	.00430	.00192	0.749
40	0.45	.50	.00831	.00362	.00230	1.11
60	0	.05	.0423	.225	.00188	0.735
60	0.45	.50	.0419	.169	.00248	1.30

An examination of Table VI brings out the following points: (1) the secondary salt effect is as predicted; (2) the velocity constants are not greatly changed by change in salt concentration. The explanation of the second fact becomes apparent on consideration of primary and secondary salt action. As  $f_0$  decreases the activity of the non-electrolyte decreases and the velocity would be expected to decrease. On the other hand,  $K_c$  increases, the hydroxyl-ion concentration increases, and the velocity would be expected to increase. Thus we have two compensating effects. It is possible that primary and secondary salt action are not essentially different in mechanism.

The temperature coefficient,  $k_{40}/k_{30}$ , was determined by the "two-thermostat" method and found to be 2.36 with the glycine-sodium hydroxide buffer when no salt was added, and 2.34 when 0.45 *N* in sodium chloride.

With the borate-sodium hydroxide buffer it is not feasible to calculate  $K_c$  in the usual way, as it is difficult to say what ions are involved. Table VII shows the change in the velocity constant with increasing salt concentration. The buffer solution used was 0.05 *M* in boric acid and 0.021 *N* in sodium hydroxide. Its Sørensen value was approximately nine. The experiments were carried out at 80°.

TABLE VII

## DECOMPOSITION OF NITROSOTRIACETONEAMINE IN BORATE BUFFER SOLUTIONS

NaCl	0	0	0.11	0.18	0.57	0.68
<i>k</i>	0.0191	0.0187	.0177	.0166	.0124	.0108

With increasing salt concentration the velocity decreases.



Incidentally, having determined the primary salt effect, the decomposition of nitrosotriacetoneamine is readily adaptable to the estimation of Sørensen values between seven and ten at temperatures above 60°

The author is indebted to Professor F. O. Rice for his kindly criticism.

### Summary

1. The catalytic decomposition of nitrosotriacetoneamine has been studied in solutions of sodium hydroxide and in alkaline buffer solutions.
2. The rates of reaction and the temperature coefficients have been determined from 20° to 80°.
3. The temperature coefficient is unaffected by neutral salt.
4. The results are in agreement with Brönsted's concept of secondary kinetic salt effect.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE JOHNS HOPKINS UNIVERSITY]

## THE CATALYTIC ACTIVITY OF DUST PARTICLES

By F. O. RICE

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When a chemical reaction proceeds in a closed vessel it is subject to two influences which can ordinarily be neglected but which in some reactions completely determine the speed, because in the absence of the particular influence the reaction will not take place at a measurable rate. The first of these influences is the surface of the containing vessel; if, as is commonly the case, this is of glass, the reaction is surrounded by a thin envelope of condensed water containing many dissolved substances the most important of which is probably the hydroxyl ion. This film catalyzes many reactions between liquids, between dissolved substances and between gases; examples such as the interconversion of liquid keto-enol isomers,<sup>1</sup> the change of *n*-nitrocamphor to the pseudo form in different solvents<sup>2</sup> and the bromination of ethylene<sup>3</sup> illustrate the important chemical effects of this surface film, since none of these reactions takes place in a vessel with non-reactive walls.

The second influence arises from the presence of finely-divided dust particles which are always present unless special precautions are taken to exclude them. If an intense beam of light be passed through air or other gas and viewed at right angles against a dark background, the path of the beam is plainly visible owing to light scattering by the great numbers of

<sup>1</sup> Meyer and Schoeller, *Ber.*, **53**, 1410 (1920). Meyer and Hopff, *Ber.*, **54**, 579 (1921).

<sup>2</sup> Lowry, *J. Chem. Soc.*, (a) **75**, 220 (1899); (b) **83**, 1316 (1903).

<sup>3</sup> Stewart and Edlund, *THIS JOURNAL*, **45**, 1014 (1923). Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).