Acknowledgment.—We wish to acknowledge our gratitude to the Graduate School of the University of Minnesota for the financial assistance which made this work possible.

Summary

1. The isoelectric point of freshly precipitated silver iodide has been found at a *p*Ag of 6.0.

2. It has been shown that freshly precipitated silver iodide at the equivalence potential (*p*Ag = *p*I = 7.83) retains an excess of iodide adsorbed, corresponding to 0.09% of the total amount of iodide in the precipitate.

3. The adsorption of silver and iodide ions by the fresh precipitate follows the expression $\Delta X = K\Delta \log C$ in the *p*Ag range between 4 and 7.2, iodide ions being more strongly adsorbed than silver ions.

4. The theoretical ratio KI:Ag is found in the potentiometric titration of silver with iodide at room temperature, if the end-point of the titration is taken at the isoelectric point (*p*Ag = 6.0), instead of at the equivalence potential, and if a correction is applied for the excess silver ions in the solution.

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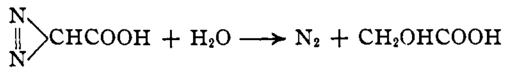
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Catalytic Decomposition of Diazoacetate Ion in Aqueous Solution[1]

BY CECIL V. KING AND EDGAR DARE BOLINGER

Solutions containing salts of diazoacetic acid were first prepared by Curtius,[2] by alkaline hydrolysis of diazoacetic ethyl ester. The salts are, he found, stable in alkaline solution, but decompose with rapid evolution of nitrogen on neutralization with even carbonic acid, indicating that the acid is unstable



Traube[3] made the sodium salt both by alkaline hydrolysis of the ester and by reduction of isonitroaminoacetic acid with sodium amalgam, and isolated the pure crystals from the solution. The preparation was further studied by Hantzsch and Lehmann[4] and by Müller,[5] who showed that the salts polymerize slowly in alkaline solution to the pseudo- or bi-diazoacetates

(or isomers)

Pure solid potassium diazoacetate is stable if kept dry, cool and in the dark. It explodes on heating or on shock.

In this research it was found possible to study the rate of nitrogen evolution when the potassium salt is dissolved in dilute alkali or in buffers of very weak acids and their salts. The reaction is exceedingly sensitive to general acid catalysis, and is of particular interest because the reaction of a negative ion with the acid catalyst is involved. So far as the authors are aware, no other case of this type has been studied. If it is assumed that the rate-controlling step in such a catalysis involves the transfer of a proton from the acid to the reacting molecule, a negative ion should be much more sensitive to such catalysis than a neutral molecule. In accordance with this supposition it is found that the hydrogen-ion catalysis of this reaction is greater than the corresponding diazoacetic ester catalysis by some ten million-fold.

The reaction is of interest, too, because it shows abnormalities of a type first observed in the basic catalysis of nitramide decomposition in *m*-cresol solution.[6] In that case catalysis by anion bases was found to vary inversely with the concentration of the corresponding acid so that it was necessary to extrapolate the molar basic constants to $1/C_{\text{acid}} = 0$ to obtain comparable values. The catalysis by the anion of the solvent was variable and much lower than the value predicted from the catalysis by other bases. The latter abnormality was also found in the nitramide catalysis in water solution, *i. e.*, catalysis by the hydroxyl ion is lower than that predicted from the other

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[1] Condensed from Master's and Doctor's theses presented by Edgar Dare Bolinger in partial fulfilment of the requirements for these degrees at New York University, in 1934 and 1936.

[2] Curtius, *Ber.*, **18**, 1283 (1885).

[3] Traube, *ibid.*, **29**, 667 (1896).

[4] Hantzsch and Lehmann, *ibid.*, **34**, 2521 (1901).

[5] Müller, *ibid.*, **41**, 3136 (1908).

[6] Brönsted, Nicholson and Delbanco, *Z. physik. Chem.*, **A169**, 379 (1934).

bases.[7,8] In the diazoacetate decomposition it has been found possible to study these abnormalities in greater detail. The catalysis by an acid decreases with increasing acid concentration, with increasing base concentration, and on addition of other acids. While it is possible to systematize these irregularities, no explanation has been found; one similar to that offered by Brönsted, Nicholson and Delbanco[6] is obviously inadequate.

In buffers of *p*H 10 or higher, the diazoacetate decomposition is strictly unimolecular. In neutral or slightly acid solutions, however, side reactions take place which increase the *p*H. The most important of these is replacement of nitrogen by the glycolic acid formed instead of water. This is analogous to the acid catalysis of nitrogen replacement by acids in the diazoacetic ester decomposition, which takes place to some extent in aqueous, but especially in non-aqueous solutions.[9]

Materials, Apparatus and Procedure

Potassium Diazoacetate.—Diazoacetic ethyl ester was hydrolyzed as described by Müller[5] by shaking with an equal weight of potassium hydroxide in 2 *M* solution. When the ester phase had just disappeared (about four hours) the solution was evaporated, as rapidly as possible, almost to dryness (at 25° *in vacuo* with an oil pump and "dry-ice" trap). The desired salt is somewhat soluble in alcohol, practically insoluble in ether; the polymer (which is formed to some extent) is practically insoluble in alcohol. Consequently the residue was extracted with alcohol and the diazoacetate precipitated by adding about 5 volumes of ether; potassium hydroxide remains in solution. This differs from Müller's method in that he recovered the salt by evaporating the solution almost to dryness, sucking off the mother liquor and washing the crystals with alcohol. This procedure, we found, almost invariably leads to a product containing 10–20% of the polymer, which seems to be formed rather rapidly in the presence of alcohol. In one preparation 22 g. of crude salt was obtained from 57 g. of diazoacetic ester, and 12 g. of pure salt was obtained on recrystallization (solution in alcohol, precipitation by adding ether). The best salt gave off 96–99% of the theoretical nitrogen on addition of acid; other samples containing 10–20% polymer were used in some of the experiments with no appreciable effect on the rate.

All water used was redistilled from acid permanganate in a quartz still. All alkaline solutions were made up free from carbonate, protected from the air with soda lime tubes, and withdrawn through side-arm burets. *Phenol* solutions were standardized by the bromate-bromide method[10] and the buffers made by mixing portions with the necessary amount of sodium hydroxide. Redistilled *piperidine* of the correct boiling point was dissolved and the solution standardized against hydrochloric acid (methyl red). All other solutions were made from C. P. or "Reagent" quality chemicals and standardized when necessary.

Apparatus.—Nitrogen evolution was followed with an apparatus similar to that used previously by Brönsted and Duus.[11] The reaction flasks were of 200-cc. capacity, and 100 cc. of solution was used in each run. The potassium diazoacetate was usually made 0.005 *M* (0.062-g. sample), although this was varied from 0.0025 to 0.01 *M* with not over 3% variation in rate constants. In very slow experiments the diazoacetate sample was dissolved, and a glass capsule containing solid oxalic acid was suspended in the flask neck; after sufficient pressure readings were obtained this was dropped in to hasten attainment of the final pressure. Since in this type of measurement the final reading is of greater importance than any other single reading, care was taken to check the final pressure over a period of several hours.

The reaction flasks were immersed in a thermostat maintained at 25 ± 0.01°. Since the manometers were not thermostated, care was taken to keep the room temperature constant to ±0.5° while readings were being made.

In a number of experiments it was necessary, as noted later, to measure the *p*H of the solutions after the decomposition. This was done with hydrogen electrodes of the Hildebrand type, the potential against a calomel half-cell being measured with a Leeds and Northrup type K potentiometer. Duplicate electrodes checked to 0.1 millivolt or less.

Velocity constants were obtained by plotting log $(a - x)$, or log (final pressure minus pressure at time t) against the time in minutes; the slope of the straight line obtained is $-1/2.303$. This method avoids errors due to lack of pressure equilibrium at the beginning of the run and was especially useful when the acidity decreased at the start and the reaction became unimolecular only after the first few minutes of the run.

Preliminary Experiments

Several experiments were made to determine whether the diazo salt contained any potassium hydroxide (especially the less pure samples), or was appreciably hydrolyzed. A solution containing 0.01 *M* phenol, 0.01 *M* phenate and a few drops of thymolphthalein solution was divided into two portions. To one, enough potassium diazoacetate to make the solution 0.005 *M* was added. No difference in color could be detected either immediately or after decomposition of some or all of the salt. Similar results were obtained when the *p*H of phosphate buffers was found to change little on addition and decomposition of the salt. When a sample of the salt was dissolved in water the *p*H rose to about ten; the *p*H, as measured with a glass electrode, did not change during the remainder of the decomposition. This could not indicate simple hydrolysis of the salt since in that case the *p*H should go back during the decomposition to that of potassium glycolate. It was caused by the initial formation of glycoylglycolate, to be described below. It can be concluded that the diazoacetic acid is at least as strong as glycolic acid, as would be ex-

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[7] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[8] Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

[9] Brönsted and Bell, *ibid.*, **53**, 2478 (1931).

[10] Treadwell and Hall, "Analytical Chemistry," 7th ed., Vol. II, John Wiley and Sons, Inc., N. Y., 1930, p. 591.

[11] Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

pected from its molecular structure. The experiments with buffers also showed that potassium hydroxide was negligible as an impurity in the samples of diazoacetate prepared.

Experimental Results

1. Hydrogen (Oxonium) Ion and Water Catalysis.—The rate in dilute sodium hydroxide was found to give a constant molar value for the hydrogen-ion catalysis between concentrations of 0.4×10^{-12} and 2.0×10^{-12} *M*. The solutions were made up as indicated in Table I, the ionic strength being kept constant at 0.105 by additions of sodium chloride. The half-time of the reaction varied from seven to fifty hours. The hydrogen-ion concentrations were calculated from the sodium hydroxide concentrations, using 1.71×10^{-14} for the ion product constant of water in sodium chloride at 0.1 μ.[12]

TABLE I

CATALYSIS BY HYDROGEN ION: 25°, 0.105 μ

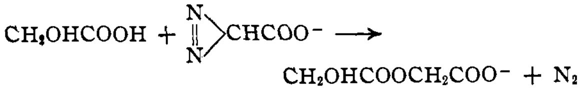
Expt.	C_{NaOH}, *M*	$C_{H_3O^+} \times 10^{12}$	$k \times 10^4$
31	0.008	2.14	7.76
27	.010	1.71	6.67
30	.0133	1.29	5.26
28	.020	0.85	3.45
29	.040	.43	2.08
32	.01	μ = .055	6.46
33	.01	μ = .015	6.22

The results are plotted in Fig. 1(A). The slope of the straight line, 3.57×10^8, is the molar catalytic constant for the hydrogen ion. The intercept, 5.5×10^{-5}, is the water constant, and when divided by the water concentration gives the molar water constant, 9.92×10^{-7}.

As shown by expts. 27, 32 and 33, catalysis in these solutions has a small, probably linear, positive salt effect amounting to 7% between $\mu = 0.015$ and 0.105.

To obtain rates at higher hydrogen-ion concentrations, pure sodium chloride solutions were used, with or without the addition of very small amounts of hydrochloric acid. In these solutions a portion of the nitrogen was evolved very rapidly; the reaction then became slower and followed the unimolecular law for the remainder of the nitrogen evolution. The *p*H rose rapidly in this first period to the neighborhood of 10. A rate curve is shown in Fig. 2, compared with a normal rate curve in a phosphate buffer whose *p*H remains constant.

This abnormality was thought at first to be due to the formation of chloroacetic acid instead of glycolic acid, since a similar side reaction occurs with diazoacetic ester.[13] However, titration of the resulting solution with silver nitrate (dichlorofluorescein as indicator) showed no loss of chloride ion. The side reaction was finally shown to be formation of glycoylglycolate ion according to the reaction



$$CH_2OHCOOH + \overset{N}{\underset{N}{\|}}\!\!>CHCOO^- \longrightarrow CH_2OHCOOCH_2COO^- + N_2$$

Glycoylglycolic acid has been prepared and studied by Wolff and Lüttringhaus.[14] It is sufficiently stable, in cold solution, to titrate quantitatively with strong bases; heating on a water-bath with excess base hydrolyzes it completely to glycolate.

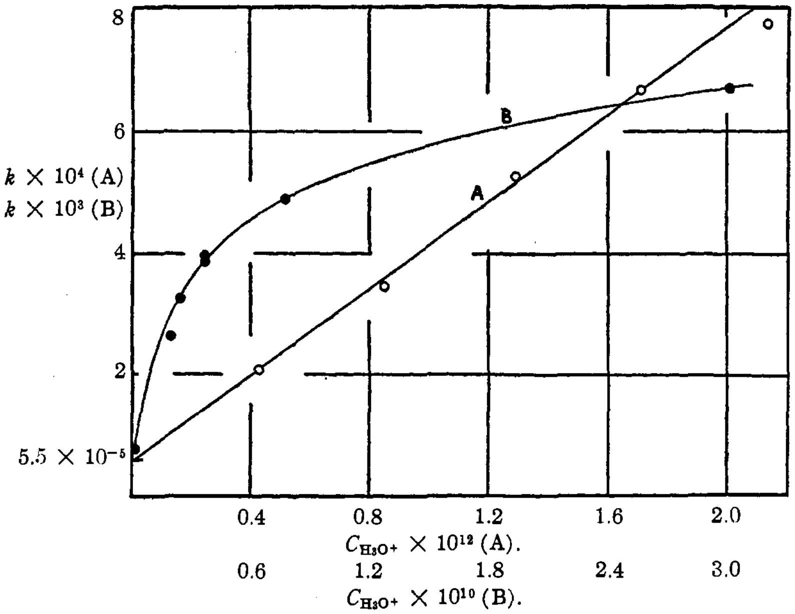


Fig. 1.—Catalysis by hydrogen ion.

The suspected formation of this ester was confirmed by experiments of the following type: 0.0005 mole of potassium diazoacetate was dissolved in 50 cc. of 0.2 *M* sodium chloride containing 0.000463 mole of hydrochloric acid. After

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[12] Harned, THIS JOURNAL, **47**, 930 (1925).

[13] Bredig and Ripley, *Ber.*, **40**, 4015 (1907).

[14] Wolff and Lüttringhaus, *Ann.*, **312**, 146 (1900).

one hour titration with sodium hydroxide showed that 0.000142 mole of acid had disappeared. A slight excess of alkali was added and the solution was heated to 90° for forty-eight hours. Titration with acid showed that 0.000142 mole of base (within experimental error) had disappeared. Heating for shorter periods (with these relatively low concentrations of reagents) showed partial return of the hydrogen ion which had disappeared initially.

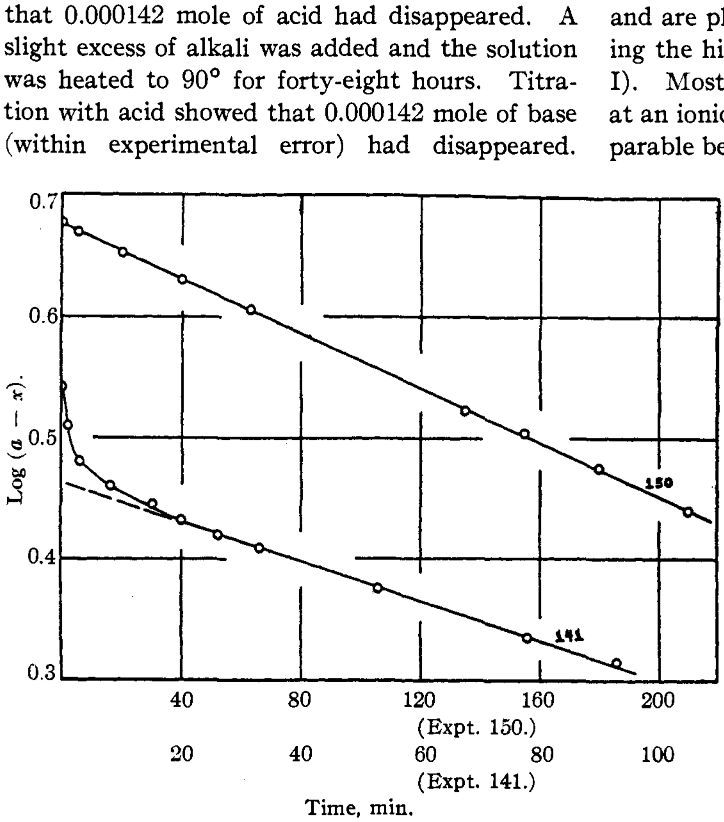

Fig. 2.—Typical time–rate curves: Expt. 150, phosphate buffer; Expt. 141, NaCl + a little HCl.

In other solutions it was found by titration that the acid disappearing corresponded roughly with the amount of nitrogen evolved in the initial rapid reaction. Consequently it seemed safe to assume that the unimolecular rate after this initial rapid reaction was a measure of the catalysis by the hydrogen ion in the final solution, as measured a few hours later with the hydrogen electrode.

These rate constants are given in Table II with the corresponding hydrogen-ion concentrations, and are plotted in Fig. 1(B), the lowest point being the highest one of Fig. 1(A), expt. 29 (Table I). Most of these experiments were carried out at an ionic strength of 0.205; the results are comparable because of the low salt effect. The molar catalysis is constant only at very low values of the hydrogen ion concentration; however, it is still of the order of 10^7 at the highest concentration used.

TABLE II

CATALYSIS BY HYDROGEN ION AT HIGHER CONCENTRATIONS

Expt.	C_{NaCl}, M	C_{HCl} added $\times 10^4$	$C_{H_3O^+}$ at end $\times 10^{12}$	$k \times 10^4$
138	0.20	1.0	20.0	26.4
140	.20	2.0	25.1	32.6
141	.20	5.0	37.4	38.4
139	.20	5.0	37.4	39.6
137	.10	0	77.6	48.9
142	.20	10.0	302	67.0

2. Phenol Catalysis.—The experiments in phenol–sodium phenate buffers are summarized in Table III; the phenol concentration is designated by C_{HP} and the sodium phenate by C_{P^-}. The ionic strength was made 0.105 in every case by suitable additions of sodium chloride. The values of k are plotted in Fig. 3; the solid lines represent the effect of keeping the buffer ratio and consequently the *p*H constant. The phenol has a decided catalytic effect; but since the curves are not straight lines, are not parallel, and do not extrapolate satisfactorily to values to be ascribed to the hydrogen ion, it is evident that the catalysis is not of a simple type. The molar phenol catalysis decreases with increasing phenate concentration. Since the hydrogen ion catalytic constant in a one-to-one phenol–phenate buffer should be only about 0.005, this effect cannot be explained entirely by repression of the hydrogen-ion catalysis by the phenate.

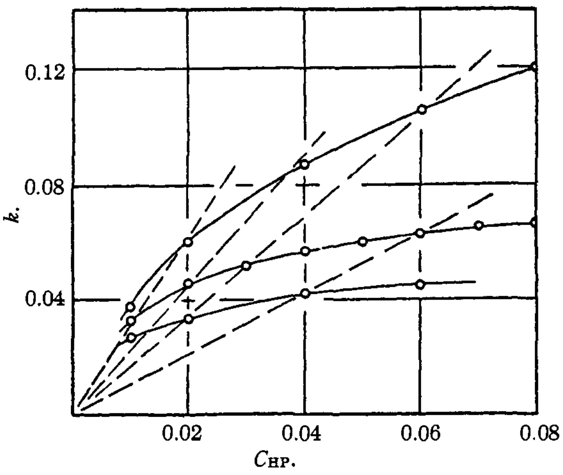

Fig. 3.—Catalysis by phenol: solid lines—constant phenol–phenate ratio; broken lines—constant phenate concentration.

The broken lines of Fig. 3 show that the molar catalysis by phenol at constant phenate concentration is approximately constant. Consequently, following the procedure of Brönsted, Nicholson and Delbanco,[6] the slopes of these lines were taken as molar constants, and plotted against $1/C_{P^-}$. The first three values (Fig. 5) lie on a straight line

$$k_m = 0.45 + 0.0344/C_{P^-}$$

The value 0.45 can be taken as the molar phenol constant at high base concentration.

TABLE III

CATALYSIS BY PHENOL: 25°, 0.105 μ

Expt.	C_{HP}, M	C_{P^-}, M	k
3	0.01	0.01	0.0325
4	.02	.02	.0456
5	.03	.03	.0515
6	.04	.04	.0570
7	.05	.05	.0604
8	.06	.06	.0631
9	.07	.07	.0660
10	.08	.08	.0664
11	.09	.09	.0675
2	.10	.10	.0690
13	.01	.015	.0264
14	.02	.030	.0332
15	.04	.060	.0420
16	.06	.090	.0451
17	.01	.005	.0371
18	.02	.010	.0600
19	.04	.020	.0872
20	.06	.030	.1055
21	.08	.040	.1202
25	.10	.050	.130
22	.01	.01	.0290 (μ = 0.015)
24	.01	.01	.0306 (μ = 0.055)

Salt effect in the phenol buffers was found to be small and probably of the linear type. It is about 12% between μ = 0.015 and 0.105, as shown by expts. 22, 24 and 3.

3. Ammonium-Ion Catalysis.—Concentrations were planned for this system to define better the effect of varying the ammonium-ion concentration at constant ammonia concentration. The details are given in Table IV and the values of k are plotted in Fig. 4. The molar catalysis constants may be represented by

$$k_m = 0.57 + 0.0274/C_{NH_3}$$

which is the equation for the straight line of Fig. 5.

There is a pronounced negative salt effect on the rate in ammonia–ammonium chloride solutions at low ionic strengths, and a number of experiments were run to investigate this. Table V gives the results, and in Fig. 6 the values of log k are plotted against $\sqrt{\mu}$. It was necessary, of course, to use a constant ammonia concentration throughout; since the secondary salt effect is small this is approximated in the solutions of Table V. At low ionic strengths the rates conform to the Brönsted requirement of a slope of −1.

TABLE IV

CATALYSIS BY AMMONIUM ION: 25°, 0.105 μ

Expt.	$C_{NH_4^+}$, M	C_{NH_3}, M	k
41	0.01	0.01	0.0163
57	.02	.02	.0260
50	.04	.04	.0420
51	.06	.06	.0593
53	.08	.08	.0766
52	.10	.10	.0833
55	.10	.10	.0813
36	.01	.02	.0154
37	.02	.04	.0243
38	.03	.06	.0297
39	.04	.08	.0363
34	.05	.10	.0422
56	.08	.16	.0597
35	.10	.20	.0658
54	.01	.03	.0137
58	.02	.06	.0214
59	.04	.12	.0314
68	.04	.12	.0348
60	.06	.18	.0438
61	.08	.24	.0523
63	.01	.04	.0127
64	.02	.08	.0201
65	.04	.16	.0303
66	.06	.24	.0411

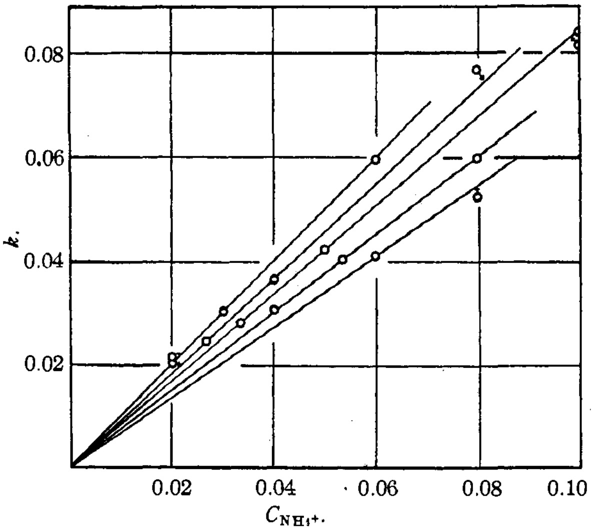

Fig. 4.—Catalysis by ammonium ion: straight lines for constant ammonia concentration.

TABLE V

SALT EFFECT IN AMMONIUM ION–AMMONIA BUFFERS

$C_{NH_4^+} = 0.005\ M$, $C_{NH_3} = 0.005\ M$, $C_{CHN_2COOK} = 0.005\ M$

Expt.	C_{NaCl}, M	μ	k
69	0	0.010	0.0131
70	0	.010	.0134
85	0	.010	.0139
71	0.005	.015	.0126
86	.005	.015	.0131
73	.010	.020	.0122
75	.015	.025	.0118
87	.020	.030	.0117
77	.025	.035	.0110
78	.025	.035	.0114
79	.045	.055	.0110
80	.045	.055	.0111
81	.065	.075	.0107
82	.065	.075	.0106
159	.120	.130	.00965
157	.150	.160	.00934
160	.290	.300	.00953
158	.490	.500	.00940
155	.490	.500	.00920

TABLE VI

CATALYSIS BY PIPERIDINIUM ION: 25°, 0.105 μ

Expt.	C_{PH^+}, M	C_P, M	$k \times 10^3$
96	0.030	0.010	2.64
95	.020	.010	2.10
114	.010	.010	1.56
116	.005	.010	1.41
108	.0125	.050	0.92
103	.025	.050	1.20
104	.050	.050	1.79
106	.100	.050	2.73
110	.025	.100	0.88
112	.050	.100	1.25
115	.100	.100	1.91
98	.050	.200	0.825
113	.075	.200	1.06
111	.100	.200	1.25

4. Piperidinium-Ion Catalysis.—The piperidinium ion is an acid of the same charge type as the ammonium ion, but is much weaker. The experiments of this series are summarized in Table VI, where the piperidine and piperidinium-ion concentrations are represented by C_P and C_{PH^+}, respectively. The rate constants are plotted in Fig. 7 where the solid and broken lines have the same significance as before. The lines for constant buffer ratios are apparently straight and extrapolate to approximately the values expected for the hydrogen-ion catalysis (see Fig. 1); but the piperidinium-ion catalysis again decreases with increasing piperidine concentration. The slopes of the broken lines are taken as molar catalysis constants for the corresponding values of the piperidine concentration, and plotted in Fig. 9 against the reciprocal of the latter. The three lowest points lie approximately on the straight line

$$k_m = 0.0060 + 0.00086/C_P$$

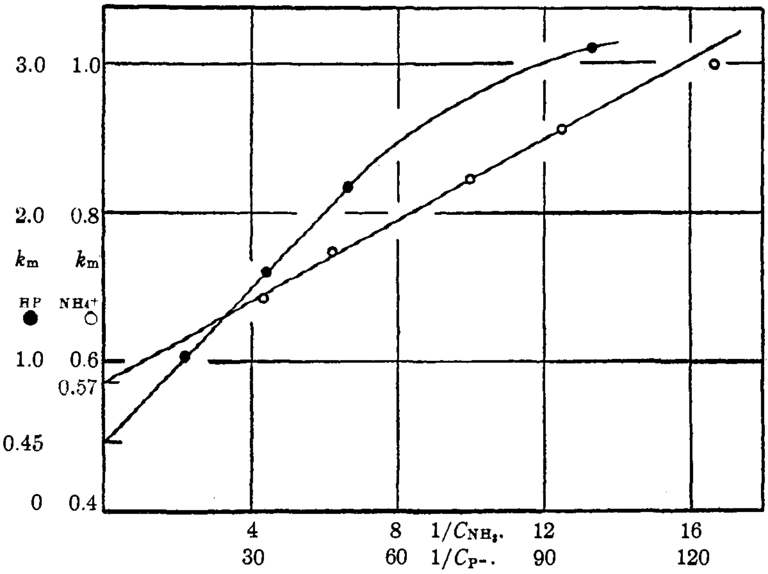

Fig. 5.—Plot of k_m *vs.* reciprocal of ammonia and phenate concentration.

5. Secondary Phosphate-Ion Catalysis.—Buffers of secondary and tertiary phosphate ions were made by adding sodium hydroxide to solutions of pure disodium hydrogen phosphate. All the experiments were carried out with the ionic strength 0.205 to make it possible to vary the ion concentrations sufficiently. Sodium sulfate was used as the inert salt to make up the ionic strength, in order to keep the valence types as nearly comparable as possible. The data are shown in Table VII and the values of k are plotted in Fig. 8. The solid curves are for constant ratios of $HPO_4^{=}$ and $PO_4^{\equiv}$ introduced into the solution rather than for the equilibrium mixtures, and this partly accounts for their slopes and lack of extrapolation to reasonable values for the hydrogen-ion catalysis. The points on the broken lines also do not represent quite the same base ($PO_4^{\equiv}$) concentrations, but this is not of great importance in analyzing the results. The slopes of the broken lines are plotted against $1/C_{PO_4^{\equiv}}$ in Fig. 9; the straight line is represented by the equation

$$k_m = 0.0050 + 0.00079/C_{PO_4^{\equiv}}$$

TABLE VII

CATALYSIS BY SECONDARY PHOSPHATE ION: 25°, 0.205 μ

Expt.	$C_{HPO_4^{--}}$, M	$C_{PO_4^{\equiv}}$, M	$k \times 10^3$
143	0.010	0.020	1.16
144	.020	.020	1.66
145	.030	.020	2.11
148	.005	.010	1.50
147	.010	.010	1.83
146	.015	.010	2.30
149	.005	.005	2.15
150	.0075	.005	2.56
151	.010	.010	1.58 (μ = 0.105)
152	.010	.010	2.15 (μ = 0.305)

This system shows a decided positive salt effect, which is to be expected theoretically. No attempt was made to study this at low ionic strengths, but expts. 151, 147 and 152 of Table VII indicate its magnitude.

6. Acetic Acid Catalysis.—The catalytic effect of acetic acid is far too great to be measured in ordinary buffers; the reaction proceeds at a measurable speed in pure sodium acetate solutions. Consequently this series was made in 0.2 M sodium acetate to which small amounts of acetic acid or sodium hydroxide were added; the pH of each solution was measured with the hydrogen electrode after the run. The acetic acid concentration was then calculated, using K_c for acetic acid = 2.18×10^{-5} in such solutions.[15] There was an initial rapid evolution of nitrogen as in the dilute hydrochloric acid solutions (Table II), though not as great; and this was accompanied by an initial rise in pH. The rates again were unimolecular during the remainder of the reaction. Data are given in Table VIII. The rate constants are corrected by subtracting values for the hydrogen-ion catalysis, estimated from the curve of Fig. 1. The validity of this procedure is rather doubtful since addition of acetic acid probably represses the hydrogen-ion catalysis somewhat; however, the correction is only about 10% of the total rate. The values of k fall reasonably well on the straight line of Fig. 10, considering the difficulties of obtaining accurate results in such solutions. The slope of this line, 1.20×10^4, is taken as the molar catalytic constant of acetic acid. The value is probably somewhat higher, however, than would be obtained for infinite acetate-ion concentration.

TABLE VIII

CATALYSIS BY ACETIC ACID: 25°, 0.205 μ

Expt.	C_{HAc}(a) or C_{NaOH}(b) added $\times 10^4$	$C_{H_3O^+} \times 10^{10}$	$C_{HAc} \times 10^6$	k	k(corr.)
131	2.0a	6.17	5.66	0.0730	0.0650
130	1.0a	4.57	4.20	.0569	.0494
128	0.1a	3.47	3.18	.0428	.0358
132	1.0b	3.31	3.04	.0451	.0383
129	..	2.72	2.50	.0368	.0302
133	4b	1.92	1.75	.0266	.0205
134	10b	1.03	0.946	.0114	.0061
136	20b	0.776	.712	.0065	.0017
135	10b	.234	.215	.00575	.0028

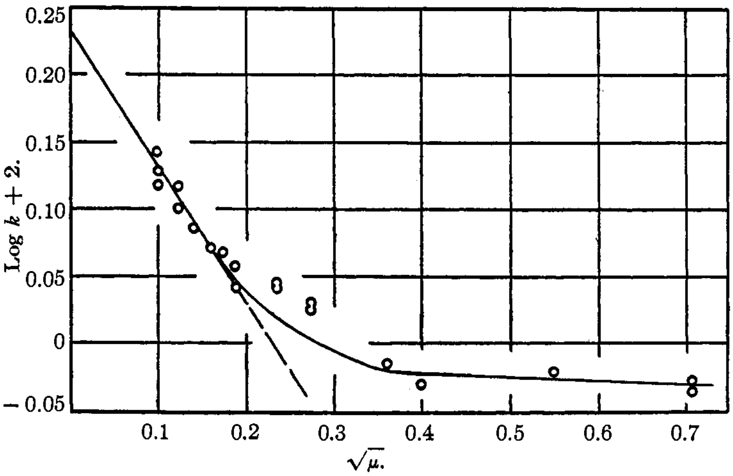

Fig. 6.—Salt effect on catalysis by ammonium ion.

Correlation and Discussion of Results

The molar catalytic constants conform well with the Brönsted expression for such catalysis.[16]

$$k_m = GK_A^x q^x p^{1-x}$$

The necessary data for applying this relation are given in Table IX. The values of k_m are those extrapolated to infinite base concentration except for hydrogen ion and acetic acid. The values of p and q are taken as the number of atoms in the acid molecule from which a proton can be detached and the number of atoms in the base molecule to which a proton can attach itself, as suggested by Pedersen.[17] Acid dissociation constants at infinite dilution are used in accordance

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[15] Cohn, Heyroth and Menkin, THIS JOURNAL, **50**, 696 (1928).

[16] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[17] Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).

with the suggestion of Pedersen that these are a better measure of the "inner acid strength" than values at finite ionic strength. Conformity to the equation is somewhat improved by these modifications.

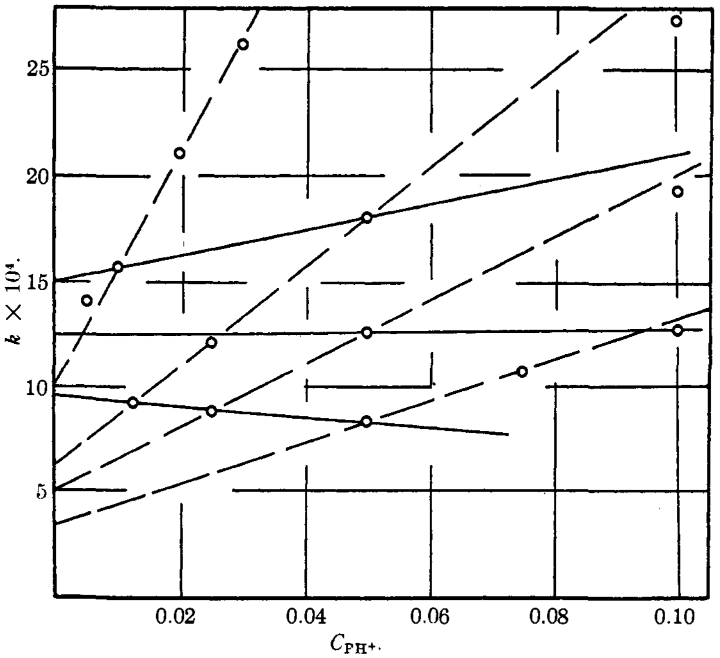

Fig. 7.—Catalysis by piperidinium ion: solid lines—constant buffer ratio; broken lines—constant piperidine concentration.

TABLE IX

THE RELATION BETWEEN VELOCITY CONSTANTS AND ACID STRENGTH

Acid	p	q	k_m	K^0_A
H_2O	1	1	9.92×10^{-7}	1.80×10^{-16}
$HPO_4^=$	1	4	0.0050	4.90×10^{-13}
$C_5H_{10}NH_2^+$	1	1	.0060	8.00×10^{-12}
C_6H_5OH	1	1	.45	1.06×10^{-10}
NH_4^+	1	1	.57	5.52×10^{-10}
$HC_2H_3O_2$	1	2	1.32×10^4	1.75×10^{-5}
H_3O^+	1	1	3.57×10^8	55.5

The values of K^0_A in Table IX for water, phenol and acetic acid were taken directly from the literature.[12,18,19] Those for piperidinium ion and ammonium ion were calculated from values for the basic constants[18] (pp. 273, 260) and Harned's value for water.[12] The value for the phosphate ion was determined from the data of Brönsted and King for the hydrolysis of the tertiary phosphate ion at 15°.[20] Their values of K_c were plotted against $\sqrt{\mu}$ and extrapolated to zero μ by drawing a straight line with the theoretical slope (-2) through the point of lowest concentration. The value obtained is probably not accurate, but seems more satisfactory than any value found in the literature. The value for the piperidinium ion was checked satisfactorily from the data of Brönsted and King.

In Fig. 11 values of log k_m/p are plotted against log (q/pK^0_A). The straight line corresponds to the equation

$$k_m/p = 1.90 \times 10^7 (q/pK^0_A)^{0.833}$$

The excellent conformity to this relation over a range of velocity constants from 10^{-6} to 10^{+8} and of dissociation constants from 10^{-16} to 10^{+2}, with such a variety of acid types, is rather remarkable. A detailed study would probably show some variation of both G and x with acid type, as in the nitramide decomposition. However, the effect of the charge type of the proton donor is small compared to that of the proton acceptor; the molar constant for hydrogen ion, 3.57×10^8, may be compared with that for hydrogen ion catalysis of diazoacetic ethyl ester decomposition, 13.6 at zero ionic strength at 15°.[21] This seems to indicate that formation of the true "critical complex" is intimately connected with the proton transfer.

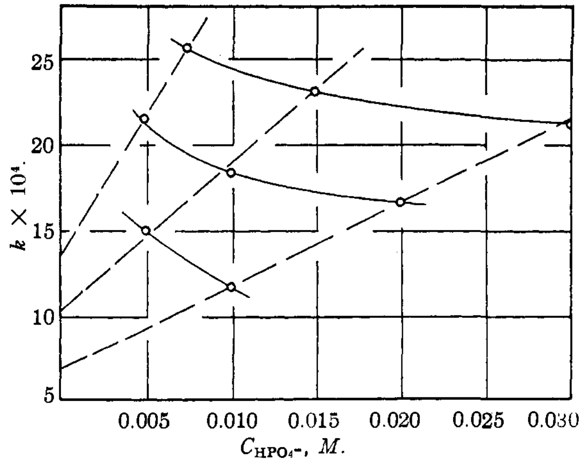

Fig. 8.—Catalysis by secondary phosphate ion.

Salt Effects and Mechanism.—It has been assumed in the preceding sections that the rate-controlling step is

$$N_2CHCOO^- + HA^z \longrightarrow \underset{\text{Intermediate Complex}}{(N_2CHCOO,HA)^{z-1}}$$

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[18] "International Critical Tables," Vol. VI, p. 271.

[19] Harned and Ehlers, THIS JOURNAL, 54, 1350 (1932); MacInnes and Shedlovsky, *ibid.*, 54, 1429 (1932).

[20] Brönsted and King, *ibid.*, 47, 2523 (1925).

[21] Guggenheim, *Phil. Mag.*, [7] 2, 538 (1926).

This is in agreement with the salt effects found. With hydrogen ion as the catalyst there should be a negative primary salt effect of the exponential type. In ordinary concentrations of a strong acid secondary salt effect would be negligible; but in the solutions used here (Tables I and II) the concentration of hydrogen ion is controlled through the equilibrium

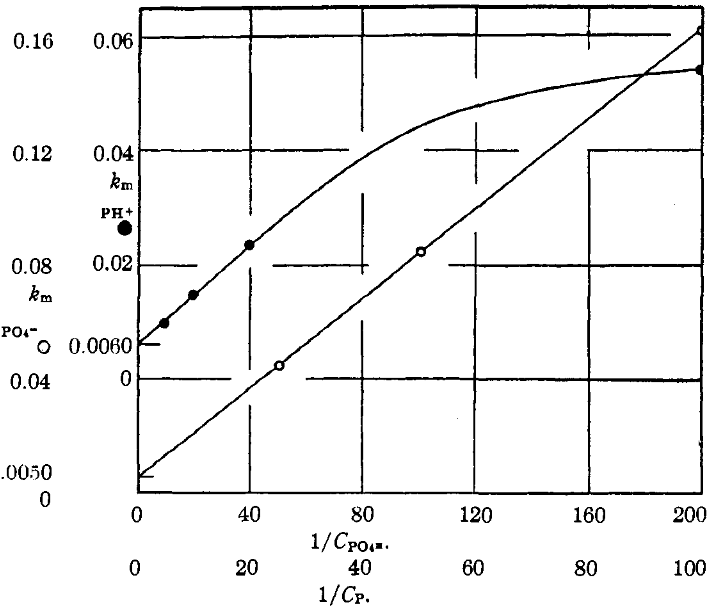

Fig. 9.—Plot of k_m *vs.* reciprocal of tertiary phosphate and piperidine concentration.

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

Since this has an exponential positive salt effect of the same magnitude as the primary salt effect, the net result is the small linear effect found.

In the phenol–phenate buffers both primary and secondary salt effects are small, the largest effect being an increase in the hydrogen-ion concentration on addition of salt. In the ammonium ion buffers, however, the primary effect is of the negative, exponential type, while the secondary effect is small. The net effect at low ionic strengths is represented by the equation

$$\log k_c = \log k_s - \sqrt{\mu} \text{ (at 25°)}$$

as shown in Fig. 6. This relation is valid over only a very limited range, however, because of the several salt effects involved.

In the secondary phosphate solutions, the primary effect is of the negative exponential type, the secondary of the positive exponential type. The secondary phosphate ion increases in concentration on addition of salt sufficiently to make the net effect positive, although the hydrogen ion decreases in concentration simultaneously.

Other possible mechanisms for the reaction would be: (1) spontaneous reaction of the undissociated acid; (2) acid catalysis of the undissociated acid reaction; and (3) base catalysis of the undissociated acid reaction. The first is excluded by the general acid catalysis. The second would be compatible with the salt effect in some of the buffer systems, but not in the sodium hydroxide solutions. For if the rate equation were

$$dx/dt = kC_{N_2CHCOOH}C_{H_3O^+}f_0f_1/f_1$$

the primary salt effect would be small; but since

$$C_{N_2CHCOOH} = K\frac{C_{N_2CHCOO^-}f_1}{C_{OH^-}f_0f_1} \text{ and } C_{H_3O^+} = \frac{K_w^0}{C_{OH^-}}\frac{1}{f_1^2}$$

the rate would be proportional to the square of the hydrogen-ion concentration and have a large exponential salt effect. The third possibility would lead, in sodium hydroxide solutions, to a rate independent of the hydroxyl-ion concentration.

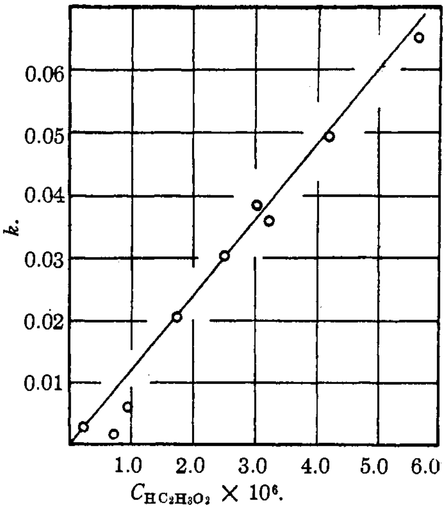

Fig. 10.—Catalysis by acetic acid.

Abnormalities.—The repressive effect of base on the acid catalysis was found in every system where the base concentration could conveniently be varied. The decreasing molar catalysis at higher acid concentration was most evident with the hydrogen ion, but sometimes appeared in the other systems. In Fig. 7 especially, all the points for the highest piperidinium-ion concentration fall below the straight lines for rates at constant base concentration. The acetic acid catalysis seems to fall off at higher concentrations, though the experimental accuracy is not great enough to warrant definite conclusions.

These abnormalities are probably generally characteristic of extremely high acid or base catalysis. In the nitramide decomposition in *m*-cresol[6] where similar effects were first found, the value of G in the Brönsted expression ($10^4 - 10^6$) is far higher than in any other case studied except the diazoacetate reaction described here. Even in the hydroxyl-ion catalysis of the nitramide decomposition in water, molar constants calculated from the data of Brönsted, Pedersen and Duus[7,11] are variable and lower than predicted from catalysis by other bases; and Marlies and La Mer[8] found, at an hydroxyl-ion concentration of 10^{-11} in hydrochloric acid solution, a molar catalytic constant 0.8×10^6 while the Brönsted relation predicts a value close to 10^9. If it were possible to measure the hydroxyl ion effect at lower concentrations, higher values would probably be found.

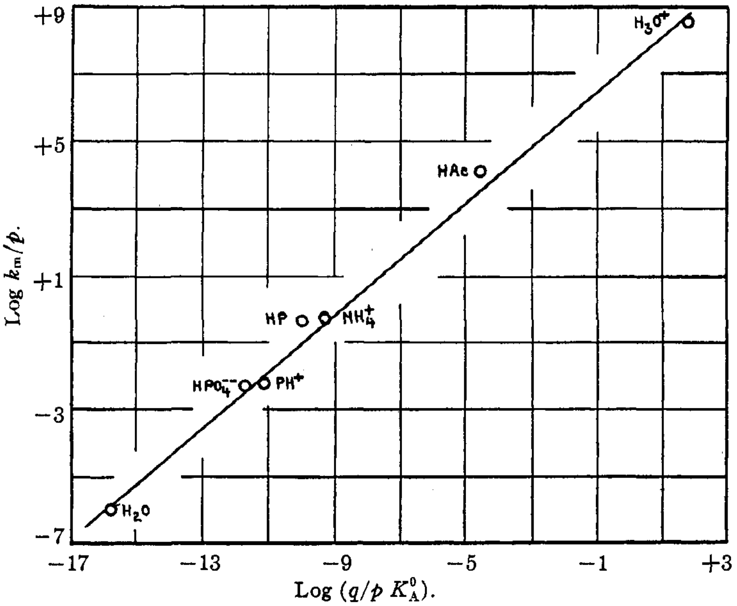

Fig. 11.—The relation between rate constants and acid dissociation constants: PH^+, piperidinium ion; HP, phenol; HAc acetic acid.

It is of interest to note that the value of x for the diazoacetate reaction, 0.833, is practically the same as that for the nitramide decomposition with some base types, both in aqueous and non-aqueous solution. This may be coincidence or may indicate a similar rate-controlling mechanism. According to the Brönsted picture the exponents for K_A and K_B should be the same for conjugate acids and bases when the rate-controlling mechanisms are similar, but this has not been found to hold for any systems studied previously.

Summary

The preparation of potassium diazoacetate, obtained by hydrolyzing diazoacetic ethyl ester, has been improved; the salt can easily be prepared free from alkali or polymerization products.

The reaction of the diazoacetate ion with water, giving nitrogen and glycolate ion, has been found to be phenomenally sensitive to general acid catalysis. The molar catalytic constant for the hydrion, 3.57×10^8 at 25°, is the highest recorded for any reaction. It may be compared with the corresponding molar constant for the decomposition of the neutral diazoacetic ethyl ester molecule, which is 13.6 at zero ionic strength at 15°. The exceptionally high rate indicates that in such catalysis the electric charge of the proton acceptor is far more important than the charge of the proton donor.

The catalysis shows abnormalities of a type found previously for the decomposition of nitramide in *m*-cresol solution. The molar catalysis constants decrease with increasing base concentration, and also with increasing acid concentration. A linear relation is found between the molar constants and the reciprocal of the base concentration except at low values of the latter.

The molar acid constants at high base concentration show excellent conformity with the equation

$$\frac{k_m}{p} = 1.90 \times 10^7 \left(\frac{q}{p} K^0_A\right)^{0.833}$$

and thus with the Brönsted theory. The value of G, 1.90×10^7 is the highest yet recorded; the value of x, 0.833, is practically the same as that found for basic catalysis of nitramide decomposition.

Salt effects in several buffer systems have been found to be in agreement with the general theory and with the mechanism postulated for this reaction.

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