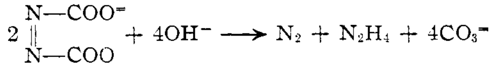
[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NEW YORK UNIVERSITY]

The Catalytic Decomposition of Azodicarbonate Ion

BY CECIL V. KING

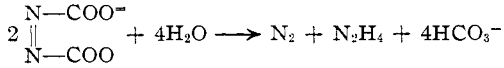
In his attempts to make diimide HN=NH, Thiele[1] prepared the potassium salt of azodicarbonic acid, by alkaline hydrolysis of azodicarbonamide. He found this salt fairly stable in alkaline solution in the cold, though it decomposes in a few minutes on heating. It is very soluble in water, but decomposes rapidly and is all gone in one to two minutes. In acid solutions the decomposition is even more rapid. Thiele found quantitative formation of nitrogen and hydrazine; the reaction takes place as follows

Alkaline solution



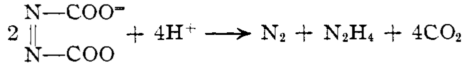
$$2\begin{matrix}\text{N—COO}^-\\ \|\\ \text{N—COO}\end{matrix} + 4OH^- \longrightarrow N_2 + N_2H_4 + 4CO_3^= \quad (1)$$

Faintly alkaline solution



$$2\begin{matrix}\text{N—COO}^-\\ \|\\ \text{N—COO}\end{matrix} + 4H_2O \longrightarrow N_2 + N_2H_4 + 4HCO_3^- \quad (2)$$

Acid solution



$$2\begin{matrix}\text{N—COO}^-\\ \|\\ \text{N—COO}\end{matrix} + 4H^+ \longrightarrow N_2 + N_2H_4 + 4CO_2 \quad (3)$$

Obviously these equations do not represent the mechanism of the decomposition; Thiele suggested the intermediate formation of diimide, which instantly gives nitrogen and hydrazine

$$2N_2H_2 \longrightarrow N_2 + N_2H_4$$

The rapid decomposition in acid solution and greater stability in basic solution suggest an acid catalyzed reaction. Preliminary study in alkaline buffers showed great sensitivity to general acid catalysis. The rate was found to be measurable in solutions of sodium hydroxide from 0.01 M to 0.10 M.

Experimental

Materials, Apparatus and Procedure

Sodium azodicarbonate was made by the method described by Thiele[1] for the potassium salt. Three preparations evolved 94, 95 and 90%, respectively, of the theoretical amount of nitrogen from acid solution. Microanalyses indicated little if any carbonate impurity, but rather some other nitrogen-containing compound.

Sodium hydroxide stock solutions free from carbonate were prepared; distilled water was not freed from carbonate since carbonate is formed in the decomposition. **Sodium acetate** buffers were made by neutralizing samples of acetic acid and adding excess sodium hydroxide. **Acetoxime** was made and purified by redistillation. Other chemicals were the best commercial grade available.

Nitrogen evolution was followed in an apparatus similar to that described by Brönsted and Duus.[2] The reaction flasks were of 100 cc. capacity and 60 cc. of solution was used for each measurement. The thermostat temperature was kept at 24.9 ± 0.02°. Since the manometers were not thermostated, the room temperature was kept constant to ±0.5° during any one experiment. In most of the experiments 73-mg. samples of azodicarbonate were used, making this concentration 0.0075 M. In all except salt effect experiments the ionic strength of the solution was kept at $\mu = 0.1225$ by addition of sodium chloride as an inert salt if necessary.

Hydrogen Ion and Water Catalysis.—In sodium hydroxide solutions, the previous considerations suggest the rate equation:

$$dx/dt = k_1 C_{N_2(COO)_2^=} C_{H_3O^+} + k_2 C_{N_2(COO)_2^=} C_{H_2O} \quad (4)$$

In all solutions used equation (1) is valid for the decomposition, *i. e.*, only carbonate ion is produced during at least the first quarter of the reaction. Also

$$C_{H_3O^+} = K_w / C_{OH^-}$$

where K_w is the ion product of water at the ionic strength in question. Neglecting the water catalysis and the change in ionic strength during reaction

$$dx/dt = kC_{N_2(COO)_2^=} \times K_w / C_{OH^-}$$

where dx/dt = moles decomposing per minute. Since two hydroxyl ions are used for each azodicarbonate ion

$$\frac{dx}{dt} = kK_w \frac{a - x}{b - 2x}$$

where a and b are initial moles of azodicarbonate and hydroxyl ion, respectively. This may be integrated to give

$$\frac{kK_w t}{2.3(b - 2a)} = \log \frac{a}{a - x} + \frac{2x}{2.3(b - 2a)} \quad (5)$$

Omission of the water catalysis term of equation (4) was found to be justified in practice. In the faster experiments it is too small to change the form of the rate equation appreciably, and in the slower experiments at higher hydroxyl ion concentrations the last term of equation (5) becomes small and the entire rate almost of the unimolecular form.

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[1] Thiele, *Ann.*, **271**, 127 (1892).

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

Rate constants were evaluated by plotting log $(a-x) - 2x/2.3\,(b - 2a)$ *vs.* t (in minutes). The negative slope of the straight line obtained, multiplied by $2.3(b - 2a)$, gives kK_w. Typical plots are shown in Fig. 1. Deviations from linearity occur for solutions of low hydroxyl ion concentration, where bicarbonate ion is formed and equation (1) is valid only near the beginning of the reaction. In this case the rate constant is obtained from the first few readings. In the special case where $b = 2a$, the rate equation becomes $kK_w = 2x/t$ and a plot of x *vs.* t should be linear. This was found true for the first few readings.

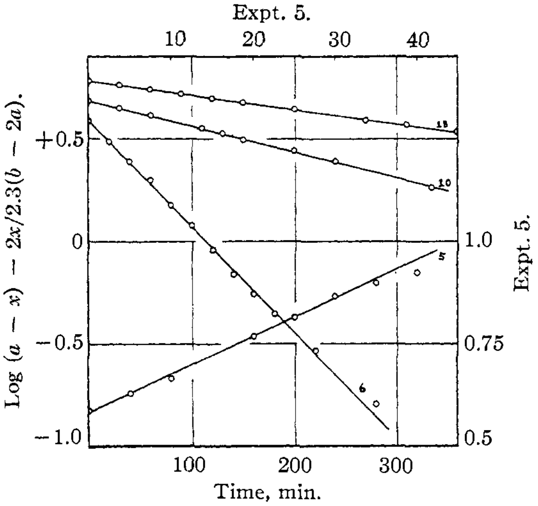

Fig. 1.—Determination of rate constants: expt. 6—divide time scale by 2, expt. 5—$(b - 2a)$ is negative.

It is evident that correct initial pressure readings must be obtained to evaluate equation (5). The azodicarbonate dissolves rapidly when dropped into the solution, and in the slower experiments no correction was necessary for slow attainment of pressure equilibrium. In the faster experiments pressure readings were taken at frequent intervals for several minutes, and an extrapolation made to an initial pressure in agreement with the rate curve.

The rate constants obtained in sodium hydroxide, with sodium chloride added to maintain a constant total ionic strength of 0.1225, are given in Table I. The increasing values of kK_w with increasing hydroxyl ion concentration are obviously due to the increasing proportion of catalysis by water. Division by the initial hydroxyl ion concentration of each experiment gives "constants," kK_w/b, which are comparable dimensionally with the unimolecular rate constants obtained in similar reactions in which the pH remains unchanged during the reaction. These values, which we shall call k', are given in Table I and plotted *vs.* hydrogen ion concentration in Fig. 2. The value of K_w used to calculate the hydrogen ion concentration was 1.665×10^{-14}, taken for $\mu = 0.1225$ from the data of Harned and Mannweiler for sodium chloride solutions.[3] This assumes K_w to be the same in sodium hydroxide and sodium chloride solutions, and also to be unaffected by the small amount of bivalent ion present.

TABLE I

CATALYSIS BY HYDROGEN ION AT 24.9°

$C_{N_2(COO)_2^=} = 0.0075\ M$ in first thirteen experiments, 0.015 M in last four. Sodium chloride added to make ionic strength 0.1225.

Expt.	C_{OH^-}, M	$C_{H_3O^+}$, $M \times 10^{13}$	kK_w	k'
5	0.01	16.65	0.0001064	0.01064
35	.01	16.65	.0001133	.01133
6	.02	8.33	.0001150	.00575
13	.025	6.66	.0001143	.00457
7	.03	5.55	.0001180	.00393
14	.035	4.76	.0001224	.00350
8	.04	4.16	.0001169	.00292
9	.05	3.33	.0001222	.00244
10	.06	2.78	.0001276	.00213
11	.07	2.38	.0001352	.00193
12	.08	2.08	.0001340	.001675
17	.09	1.85	.0001279	.001421
18	.10	1.67	.0001385	.001385
15	.025	6.66	.0001242	.00497
16	.03	5.55	.0001282	.00421
19	.035	4.76	.0001323	.00378
20	.04	4.16	.0001369	.00342

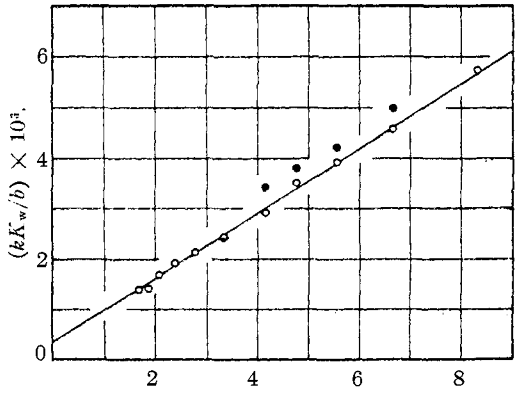

Fig. 2.—Hydrogen ion and water catalysis.

The position of the straight line of Fig. 2 was determined by the method of least squares. Its equation is

$$k' = (3.287 \times 10^{-4}) + (6.388 \times 10^{9}\ C_{H_3O^+}) \quad (6)$$

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[3] Harned and Mannweiler, THIS JOURNAL, **57**, 1873 (1935).

The slope is the molar hydrogen ion catalytic constant, $k_m(H_3O^+) = 6.39 \times 10^9$, and the intercept gives the water catalysis constant, $k_{H_2O} = 3.29 \times 10^{-4}$. The latter value divided by the water concentration gives the molar water constant, $k_m (H_2O) = 5.92 \times 10^{-6}$.

Salt Effect.—Experiments 15, 16, 19 and 20 (Fig. 2) were run with 0.015 *M* sodium azodicarbonate instead of 0.0075 *M* as in all other experiments, while the ionic strength remained 0.1225 as before. That the higher values of k' are due to specific salt effects rather than lack of validity of equation (5) is indicated by the experiments of Table II, in which 0.02 *M* sodium hydroxide was used throughout and sodium chloride and sodium sulfate added to increase the ionic strength. Values of k' are plotted in Fig. 3 *vs.* ionic strength; bivalent ions apparently exert a smaller negative salt effect than univalent ions. The type and magnitude of the salt effect are in agreement with the Brönsted theory, but the smaller effect of bivalent ions must be ascribed to the peculiarities of this particular case.

TABLE II

THE EFFECT OF IONIC STRENGTH. $C_{NaOH} = 0.02\ M$, $C_{N_2(COO)_2^-} = 0.0075\ M$; 24.9°

C_{NaCl}, *M*	μ	k'
0	0.0425	0.00667
0	.0425	.00661
0.04	.0825	.00613
.08	.1225	.00575
.12	.1625	.00547
.12	.1625	.00577
.16	.2025	.00551
$C_{Na_2SO_4}$, *M*	μ	k'
0.0133	0.0825	0.00637
.0267	.1225	.00598
.04	.1625	.00587
.0533	.2025	.00558

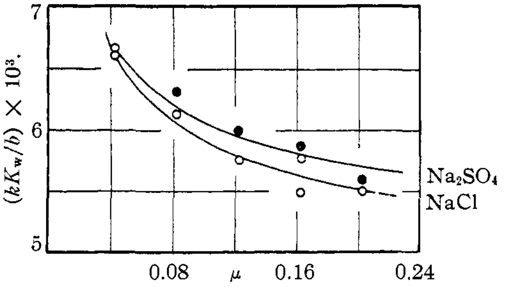

Fig. 3.—Salt effect.

Catalysis by Acetic Acid.—Rate constants in solutions of sodium hydroxide and sodium acetate were found to be appreciably higher than in sodium hydroxide and sodium chloride of the same ionic strength. If we assume no change in K_w and the same primary salt effect, the increase may be ascribed to catalysis by molecular acetic acid. Several experiments are detailed in Table III. The acetic acid concentration (C_{HAc}) was calculated from the equation

$$C_{HAc} = \frac{K_w}{K_{HAc}} \frac{C_{Ac^-}}{C_{OH^-}}$$

where $K_w = 1.665 \times 10^{-14}$ ($\mu = 0.1225$) and $K_{HAc} = 2.87 \times 10^{-5}$ at this ionic strength.[4] Values of the hydrogen ion and water catalysis calculated from equation (6) are subtracted from k' to give $\Delta k'$.

TABLE III

CATALYSIS BY ACETIC ACID: $C_{N_2(COO)_2^-} = 0.0075\ M$, $\mu = 0.1225$, 24.9°

C_{NaOH}, *M*	C_{NaAc}, *M*	C_{HAc}, *M* $\times 10^9$	k'	$\Delta k'$	k_m (HAc) $\times 10^{-5}$
0.01	0.09	5.49	0.01185	0.00088	1.60
.01	.09	5.49	.01259	.00162	2.98
.01	.09	5.49	.01190	.00093	1.70
.02	.08	2.44	.00627	.00064	2.62
.02	.08	2.44	.00593	.00030	1.23
.02	.08	2.44	.00594	.00031	1.27
					Av. 1.90

Since the acetate ion concentration remains sensibly constant during the decomposition when hydroxyl ion is present in excess, the rate equation for these solutions has the same form as equation (5). The molar catalytic constants obtained are not very accurate or even consistent, largely because the entire error of each determination is included in the relatively small increase in rate. The average value of Table III, k_m (HAc) $= 1.9 \times 10^5$, may be regarded as an approximation for the acetic acid catalysis.

Ammonium Ion Catalysis.—Catalysis by ammonium ion was measured similarly by adding ammonia to sodium hydroxide solutions and noting the increase in rate. Assuming that the ammonia present does not affect the ionization of water or the primary salt effect, this increase may be ascribed to the ammonium ion. Since the ammonia concentration is little changed during the decomposition if excess hydroxyl ion is present, the rate equation again has the same form as equation (5). The ammonium ion concentration can be calculated from $C_{NH_4^+} = K_{NH_3}C_{NH_3}/C_{OH^-}$, using $K_{NH_3} = 3.95 \times 10^{-5}$ at this ionic strength.[5]

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[4] Harned and Hickey, THIS JOURNAL, **59**, 1284 (1937).

[5] Harned and Robinson, *ibid.*, **50**, 3157 (1928).

The rates obtained are given in Table IV. Again the rate increases are erratic since the entire error falls on the increase. The average value k_{m} (NH_4^+) = 7.3 is taken as the molar catalytic constant.

TABLE IV

CATALYSIS BY AMMONIUM ION: $C_{N_2(COO)_2^{=}} = 0.0075\ M$, $\mu = 0.1225$, 24.9°

C_{NaOH}, M	$C_{\mathrm{NH_3}}$, M	$C_{\mathrm{NH_4^+}}$, M $\times 10^4$	k'	$\Delta k'$	k_{m} (NH_4^-)
0.02	0.12	2.37	0.00713	0.00148	6.24
.02	.12	2.37	.00674	.00107	4.60
.02	.09	1.78	.00736	.00171	9.60
.02	.09	1.78	.00655	.00088	5.06
.02	.06	1.19	.00630	.00065	5.46
.02	.06	1.19	.00677	.00110	9.41
.02	.03	0.59	.00575	.00010	1.70
.02	.03	.59	.00624	.00057	10.0
.01	.12	4.74	.01507	.00410	8.65
.01	.06	2.37	.01415	.00318	13.4
					Av. 7.4

Catalysis by Acetoxime.—The molar catalysis by an acid as weak as acetoxime should be much smaller than that by acetic acid or ammonium ion, but on the other hand higher concentrations of molecular acid (HA) can be maintained in the alkaline solutions necessary. Equation (5) is unusable in this case, since both hydroxyl ion and the weak acid anion decrease in concentration as the reaction proceeds. The correct rate equation

$$dx/dt = C_{N_2(COO)_2^{=}}\,(k_1C_{H_3O^+} + k_2C_{H_2O} + k_3C_{HA})$$

cannot easily be transformed into usable form even if the water catalysis be neglected. Fortunately this equation approaches the unimolecular form; it can be seen from the expression

$$C_{HA} = \frac{K_w}{K_{HA}}\,\frac{C_{A^-}}{C_{OH^-}}$$

that since both C_{A^-} and C_{OH^-} are diminishing, C_{HA} remains relatively constant and $C_{H_3O^+}$ increases less than in the preceding cases. Satisfactory "unimolecular" rate constants can be obtained by plotting log $(a - x)$ *vs.* t; in some cases the plot is perfectly linear over two-thirds of the reaction and in other cases the slope near the beginning of the reaction can be used.

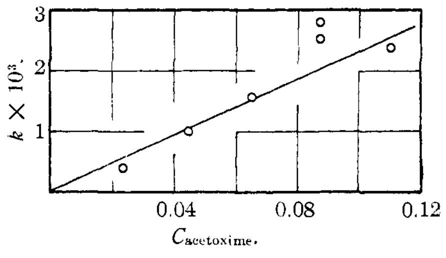

Fig. 4.—Catalysis by acetoxime.

TABLE V

CATALYSIS BY ACETOXIME: $C_{N_2(COO)^=} = 0.0075\ M$, $\mu = 0.1225$, 24.9°, $K_{HA} = 6.0 \times 10^{-13}$

Initial C_{NaOH}, M	Initial $C_{\mathrm{Acet.}}$, M	C_{OH^-} M	C_{HA}, M	$k_{\mathrm{uni.}}$	$k_{H_3O^+,\,H_2O}$	k_{HA}
0.05	0.05	0.0226	0.0226	0.00546	0.00508	0.00038
.05	.075	.0193	.0443	.00690	.00590	.00100
.05	.10	.0150	.0650	.00905	.00749	.00156
.05	.125	.0121	.0871	.01173	.00921	.00252
.05	.125	.0121	.0871	.01202	.00921	.00281
.05	.15	.0100	.1100	.01346	.01108	.00238

Rate constants obtained in this manner are given in Table V. Hydroxyl ion and unneutralized acetoxime concentrations were calculated using $K_{HA} = 6.0 \times 10^{-13}$, a value calculated by Scudder[6] for 25° from measurements of Lundén on the rate of ethyl acetate hydrolysis in barium hydroxide partly neutralized by acetoxime.[7] Values of k', called $k_{H_3O^+,\,H_2O}$ in Table V, were calculated for these hydroxyl ion concentrations from equation (6). The acetoxime constants, k_{HA}, are plotted *vs.* C_{HA} in Fig. 4, and the slope of the straight line is taken as the molar catalytic constant, k_{m} (HA) = 0.023.

It is doubtful whether the value $K_{HA} = 6.0 \times 10^{-13}$ is correct under the experimental conditions here, or whether a more satisfactory value could be calculated from Lundén's experimental results. Use of a smaller value for K_{HA} and a larger value for K_w leads to a somewhat better linear relation in Fig. 4, but due to lack of more precise rate measurements and probable complications of a type to be described later, it seems better to accept the above value as approximately correct.

Catalysis by Maltose.—In solutions containing maltose the rate is also approximately of the unimolecular form. Some difficulty arose from slow decomposition of the maltose; while it was usually unnecessary to take pressure readings for more than sixty minutes, over a period of several hours the solutions turned brown, and final pressure readings were one to five millimeters higher than usual. Since this led to rate constants that were evidently too low, new values of the rate constants were calculated using for the total pressure rise the average for preceding experiments in which the same azodicarbonate sample was used. This gives fairly consistent results, but of course introduces some error.

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(6) Scudder, "Conductivity and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1914.

(7) Lundén, *Z. physik. Chem.*, **54**, 532 (1906).

Rate constants so determined are given in Table VI, together with the calculated hydroxyl ion and unneutralized maltose concentrations, hydrogen ion and water catalysis calculated from equation (6), and finally the maltose catalysis constants. The latter are plotted *vs.* unneutralized maltose concentrations in Fig. 5, and the slope of the straight line is taken as the molar catalysis constant, k_m (HM) = 0.038.

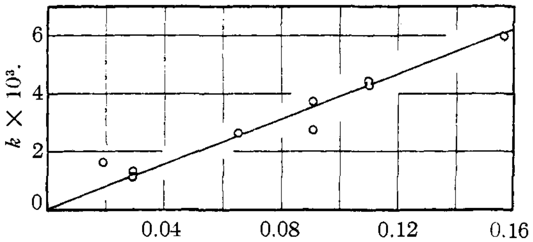

Fig. 5.—Catalysis by maltose.

TABLE VI

CATALYSIS BY MALTOSE: $C_{N_2(COO)_2^=}$ = 0.0075 *M*, μ = 0.1225, 24.9°, K_{HM} = 1.4 × 10^{-12}

Initial C_{NaOH}, *M*	Initial $C_{Malt.}$, *M*	C_{OH^-}, *M*	C_{HM}, *M*	$k_{uni.}$	$k_{H_3O^+, H_2O}$	k_{HM}
0.05	0.05	0.0174	0.0174	0.00753	0.00590	0.00163
.10	.10	.0261	.0261	.00512	.00400	.00112
.10	.10	.0261	.0261	.00529	.00400	.00129
.10	.15	.0128	.0628	.00989	.00724	.00265
.10	.18	.0094	.0894	.01329	.00958	.00371
.10	.18	.0094	.0894	.01231	.00958	.00273
.10	.20	.0079	.1079	.01564	.01119	.00445
.10	.20	.0079	.1079	.01548	.01119	.00429
.10	.20	.0079	.1079	.01546	.01119	.00427
.10	.25	.0056	.1556	.02151	.01553	.00598

In calculating the values of Table VI, the dissociation constant of maltose was taken as 1.4 × 10^{-12}. This is somewhat lower than the value determined by Michaelis and Rona[8] at 18°, namely, 1.8 × 10^{-12}. Use of the latter value changes the position of the catalytic constants so that, in Fig. 5, no satisfactory straight line can be drawn through them and through the origin. In general too high values of the dissociation constant lead to a curve which is concave downward, too low values to a curve concave upward. The change is not sensitive enough for accurate estimation of the dissociation constant.

Catalysis by Sucrose.—In mixtures of sodium hydroxide and sucrose, the rate is again "unimolecular" over the first portion of the decomposition. Three series of experiments were run: (a) various concentrations of sucrose were added to 0.03 *M* sodium hydroxide, thus maintaining the total base concentration (C_{OH^-} + C_{S^-}) constant; (b) solutions were made up at nearly constant hydroxyl ion concentration (or *p*H) with varying sucrose concentrations; and (c) the total base concentration was kept at 0.06 *M*. In each case the ionic strength was kept at 0.1225 by addition of sodium chloride where necessary. Details are given in Table VII, where hydroxyl ion and unneutralized sucrose concentrations are given, then rate constants, hydrogen ion and water catalysis calculated from equation (6), and finally the portion of the total catalysis due to sucrose. Hydroxyl ion concentrations were calculated using K_{HS} = 2.4 × 10^{-13} for the sucrose dissociation constant, a value determined by Michaelis and Rona[8] by hydrogen electrode measurements in sodium hydroxide–sucrose mixtures with an ionic strength about 0.1 at 18°. This is based on a value of K_w = approximately 10^{-14}, and is larger than the older value found for 25° by Madsen[9] from the rate of ethyl acetate hydrolysis in such mixtures at an ionic strength of 0.0245 and again based on K_w = 10^{-14}. Experiments under way in this Laboratory show that this constant is at least as high as 2.4 × 10^{-13} at μ = 0.1225; and smaller values lead to unreasonably high values for the molar catalysis constant of sucrose.

TABLE VII

CATALYSIS BY SUCROSE: $C_{N_2(COO)_2^=}$ = 0.0075 *M*, μ = 0.1225, 24.9°, K_{HS} = 2.4 × 10^{-13}

Initial C_{NaOH}, *M*	Initial $C_{sucrose}$, *M*	C_{OH^-} *M*	C_{HS}, *M*	$k_{uni.}$	$k_{H_3O^+, H_2O}$	k_{HS}
0.03	0.05	0.0192	0.0392	0.00644	0.00587	0.00057
.03	.05	.0136	.0836	.01025	.00815	.00210
.03	.10	.0136	.0836	.01047	.00815	.00232
.03	.10	.0136	.0836	.01047	.00815	.00232
.03	.125	.0118	.1068	.01185	.00934	.00251
.03	.15	.0104	.1304	.01392	.01056	.00336
.03	.20	.0084	.1784	.01754	.01300	.00454
.03	.20	.0084	.1784	.01764	.01300	.00464
.02	.0373	.0138	.0311	.00891	.00804	.00087
.02	.0373	.0138	.0311	.00886	.00804	.00082
.04	.1616	.0133	.1349	.01097	.00833	.00264
.04	.1616	.0133	.1349	.01074	.00833	.00241
.05	.223	.0135	.1865	.01068	.00821	.00247
.05	.223	.0135	.1865	.01064	.00821	.00243
.05	.223	.0135	.1865	.01081	.00821	.00260
.06	.2716	.0141	.2257	.01049	.00787	.00262
.06	.2716	.0141	.2257	.01083	.00787	.00299
.06	.15	.0228	.1128	.00647	.00500	.00147
.06	.20	.0183	.1583	.00794	.00614	.00180

The catalysis constants are plotted in Fig. 6 *vs.* the unneutralized sucrose concentration. The molar catalysis is constant for each total base concentration, but is not constant at constant hydroxyl ion concentration, the actual catalytic

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(8) Michaelis and Rona, *Biochem. Z.*, **49**, 232 (1913).

(9) Madsen, *Z. physik. Chem.*, **36**, 290 (1901); Scudder, *loc. cit.*

effect of sucrose seeming to approach a limiting upper value in series (b). A plot of the molar constants (slopes of solid and broken straight lines of Fig. 6) *vs.* the reciprocal of the sucrate ion concentration is not linear, and probably extrapolates to zero at infinite base concentration.

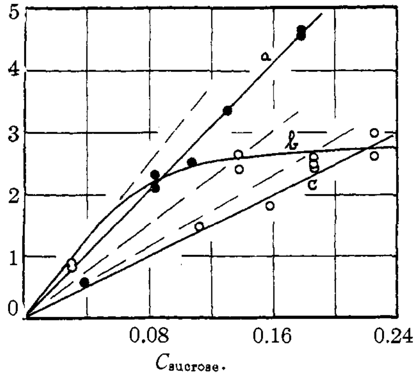

Fig. 6.—Catalysis by sucrose: (a) $C_{OH^-} + C_{S^-} = 0.03\ M$, (b) C_{OH^-} nearly constant, (c) $C_{OH^-} + C_{S^-} = 0.06\ M$.

The abnormalities of this catalysis are similar to those in the acid catalysis of diazoacetate ion decomposition[10] and in the nitramide decomposition in *m*-cresol.[11] Similar abnormalities would probably appear in the catalysis by maltose, acetoxime and the other acids if they were studied in more detail. Due to lack of accurate dissociation constants for these very weak acids and the relative inaccuracy of rate constant measurements, it seems impractical to make a more detailed study at this time.

For the present purpose we shall use as the molar catalytic constant for sucrose the value obtained with 0.06 *M* sodium hydroxide solutions, k_m (HS) = 0.0125.

Comparison of Rate Constants with Acid Strengths.—In Fig. 7 values of log k_m/p are plotted *vs.* log $(q/p\ K^0_A)$, where p and q are used as suggested by Pedersen and K^0_A is the acid dissociation constant at zero ionic strength (where this is known) (see ref. 10). In this case p and q are always 1, except for acetic acid, where q is 2.

TABLE VIII

THE RELATION BETWEEN VELOCITY CONSTANTS AND ACID STRENGTH

Acid	k_m	K^0_A
H_3O^+	6.39×10^9	55.5
$HC_2H_3O_2$	1.9×10^5	1.75×10^{-5}
NH_4^+	7.4	5.5×10^{-5}
Maltose	3.8×10^{-2}	(1.4×10^{-12})
Acetoxime	2.3×10^{-2}	(6.0×10^{-13})
Sucrose	1.25×10^{-2}	(2.4×10^{-13})
H_2O	5.92×10^{-6}	1.80×10^{-16}

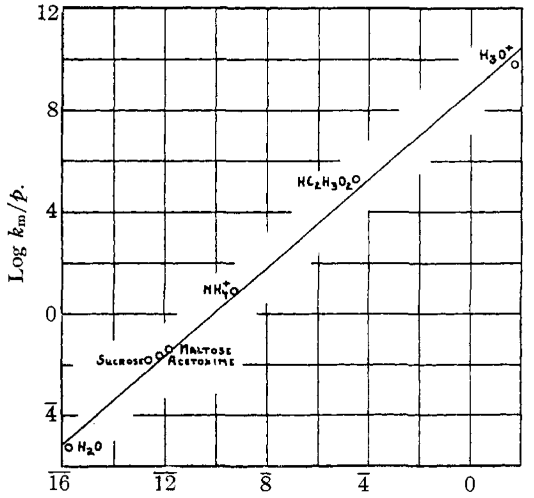

Fig. 7.—The relation between rate constants and acid dissociation constants.

The rates show satisfactory agreement with the Brönsted theory for general acid catalysis. Points on the straight line of Fig. 7 are represented by the equation

$$k_m/p = 7.40 \times 10^8 (q/pK^0_A)^{0.86}$$

Discussion.—This reaction is more sensitive to acid catalysis than any previously studied. The water catalysis is six times as great and the hydrogen ion catalysis eighteen times as great as in the diazoacetate ion catalysis.[10] The value of the constant G in the Brönsted equation (7.40×10^8) is thirty-nine times as great. On the other hand, the exponent, 0.86, is similar to the value found in several other cases.

This high sensitivity is probably largely due to the double negative charge of the azodicarbonate ion, which increases its ability to capture a proton from the catalyzing acid. While little definite evidence is available, one should expect the nitrogen–carbon bond of the azodicarbonate to be inherently more stable than that of the diazoacetate, from a comparison of the spacial relationships in the two ions, for example. The azodicarbonate is more thermostable: the diazoacetate explodes vigorously on heating or even with friction in the cold; the azodicarbonate decomposes less vigorously on heating to a somewhat higher temperature. Further, the diazoacetate poly-

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[10] King and Bolinger, THIS JOURNAL, **58**, 1533 (1936).

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

merizes readily in solution, probably through rupture of a nitrogen–carbon bond, while this behavior is not shown by the azodicarbonate.

Consequently the actual increase in sensitivity to acid catalysis due to the double negative charge may well be much greater than shown by simple comparison of these two cases. It is significant that the positively charged hydrogen ion shows three times as great an increase in catalytic effect as the neutral water molecule. The effect of the charge of the catalyzing acid has been discussed in detail by Pedersen.[12]

The strength of azodicarbonic acid cannot be estimated easily, because of its instability and the nature of the decomposition products. It is almost certainly too strong to allow appreciable amounts of the acid ion or molecular acid to exist in the alkaline solutions used here. The general acid catalysis excludes spontaneous decomposition of traces of acid or acid ion as the mechanism of the reaction; but spontaneous decomposition of small amounts of equimolecular ion-acid compounds in equilibrium with the components would be indistinguishable from the bimolecular mechanism postulated. Neither mechanism accounts for the depressing effect of bases on the molar acid catalysis, found here for sucrose and in the diazoacetate decomposition for other acids.

The author is indebted to Mr. Lewis Appleton, who carried out some of the experimental work reported here.

Summary

The decomposition of azodicarbonate ion to give nitrogen, hydrazine and carbon dioxide or carbonate ion, has been found to be extremely sensitive to general acid catalysis. It is catalyzed by water, hydrogen ion and other acids in accordance with the equation $dx/dt = C_{N_2(COO)_2^{-}}(k_1C_{H_3O^+} + k_2C_{H_2O} + k_3C_{HA} + \ldots)$. That this equation does not completely explain the mechanism is shown by the fact that the molar catalysis by sucrose (and probably by other weak acids) is diminished by bases (hydroxyl ion, sucrate ion, etc.).

The molar catalysis constants as evaluated show good agreement with the Brönsted equation $k_m/p = G(q/pK_A^0)^x$ where $G = 7.40 \times 10^8$ and $x = 0.86$. This value of G is the highest yet found for acid catalysis; the value of x is similar to that found in several other cases.

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

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Photochemical Oxidation of Hydrogen[1]

BY HILTON A. SMITH AND A. NAPRAVNIK

There have been reported three earlier studies[2,3,4] of the photochemical oxidation of hydrogen by light of wave length 1719–1725 Å. The first of these papers dealt with the over-all temperature coefficient of the reaction, while the other two resulted from studies of the individual products obtained, and the quantum yields of these products at room temperatures. The present paper reports the quantum yields of the individual products at elevated temperatures as well as additional room temperature data.

Experimental

In the last of the papers mentioned above, it was demonstrated that the reaction products were ozone, hydrogen peroxide, and water. Analysis of this mixture was carried out by pumping the exit gases from the reaction cell through an analyzing bubbler, after which they were dried and returned to the cell. Three successive runs were made on each hydrogen–oxygen mixture. During the first run the bubbler contained titanium sulfate solution. The hydrogen peroxide formed was absorbed in this solution and determined colorimetrically. During the second run the bubbler contained neutral potassium iodide solution. This absorbed both hydrogen peroxide and ozone. The bubbler liquid subsequently was acidified and the liberated iodine titrated with sodium thiosulfate. The yield of ozone was calculated by subtracting from this result the yield of hydrogen peroxide determined in the first run. Finally, a much longer run was made, again using potassium

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[1] Presented at the Boston meeting of the American Chemical Society, September 12, 1939.

[2] Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[3] Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

[4] Smith and Kistiakowsky, *ibid.*, **57**, 835 (1935).