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The Catalytic Decomposition of Nitramide in Acid and Salt Solutions[1]

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Introduction

Brönsted developed his important theory of generalized basic catalysis from his kinetic studies of the reaction

$$NH_2NO_2 \text{ (nitramide)} \longrightarrow H_2O + N_2O\text{[2]}$$

The reaction proceeds to completion without the complications of side reactions or any change in environment in aqueous systems[2b,3,4,5,6,7,8] and may be followed by physical means. The simplicity of the products and the sensitivity of the reaction to catalytic influence renders it particularly valuable for elucidating the theory of chemical kinetics in its various aspects, especially protolytic reactions. However, the difficulties of preparation and storage of nitramide have prevented the exhaustive investigation which the reaction deserves. A study of the preparation and the measurement of the decomposition of nitramide was accordingly undertaken to render this desirable reaction more conveniently available for kinetic investigations.

When this study was begun in 1929, the published work of Brönsted and his students[2b,4,5] showed that the decomposition of nitramide exhibited only generalized base catalysis, without appreciable primary salt effect. On the other hand, the other two well-established examples of generalized base catalysis, namely, the mutarotation of glucose[9] and the acetone–iodine reaction,[10] exhibited generalized acid catalysis as well. Other objectives were consequently the search for and the exact investigation of an acid catalysis and a salt effect for the nitramide reaction.

Using ordinary technique and methods of purification, an acid catalysis was quickly discovered, but the velocity constants obtained in duplicate experiments showed wide variations (5–10%). This same range of values was obtained by Brönsted and his students in their work on nitramide, but was by no means precise enough for the purpose, due to the small magnitudes of the acid and salt constants. By refining the technique the deviation from the mean was reduced to less than 1%. The first group of experiments (42 in number) in which the precision technique was not used and for which the variation in results was considerable are not reported.

Surprisingly few reactions even in solution have been measured within 1%. Furthermore, in practically all these cases a chemical method of following the reaction was used, which is surprising in view of the many advantages of physical methods.

A few experiments were made in low concentration of deuterium oxide (heavy water) and a marked decrease in rate was found (February, 1934). Further investigation in heavy water should throw light on the mechanism of the decomposition, which is still not certain, and the catalytic action of deuterium.

Materials

Nitramide.—Several modifications were made of the synthesis described by the discoverers, Thiele and Lachman.[3] The most important involves the manner of extraction of the nitramide from the aqueous solution in which it is made.[11] Other attempted methods of preparation, such as addition of silver nitrite to chloramine (explosion occurred) or addition of hydrogen chloride to an ether suspension of potassium nitrocarbamate, resulted in little or no yield of nitramide.

Further purification[5] of the nitramide produced no change in the velocity constants. The nitramide was stored in an open vessel in a desiccator over phosphorus pentoxide in the refrigerator. The desiccator was always brought to room temperature before opening to prevent condensation of moisture on the inside. The nitramide was handled exclusively in glass or bright platinum, as it attacks brass and other base metals.

Water.—Conductance water, prepared so as to ensure the absence as far as possible of all bases, *e. g.*, carbonates, silicates, etc., was used. In the last two distillations scrap platinum was used to prevent bumping, and the distillate was collected hot, a large proportion being allowed to escape as steam. The final distillation was from a quartz still.

Hydrochloric Acid.—Constant boiling hydrochloric acid was prepared from specially purified reagents. The con-

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(1) This paper was presented at the New York Meeting of the American Chemical Society, April, 1935.

(2) (a) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); (b) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

(3) Thiele and Lachman, *Ann.*, **288**, 267 (1895).

(4) Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

(5) Brönsted and King, THIS JOURNAL, **49**, 193 (1927).

(6) Brönsted and Volqvartz, *Z. physik. Chem.*, **A155**, 211 (1931).

(7) Brönsted and Vance, *ibid.*, **A163**, 240 (1933).

(8) Brönsted, Nicholson and Delbanco, *ibid.*, **A169**, 379 (1934).

(9) Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

(10) Dawson and Lowson, *J. Chem. Soc.*, 1217 (1929).

(11) Marlies and La Mer, THIS JOURNAL, **57**, 2008 (1935). The modified method will be described in full in "Inorganic Syntheses."

centrations of acid were calculated from Bonner and Wallace's tables.[12]

Potassium and sodium chlorides were recrystallized from laboratory distilled water, constant boiling hydrochloric acid and conductance water. The dried salt was fused in a platinum crucible, the melt poured onto a wide platinum dish, broken up and bottled while hot.

Nitrous oxide, stated by the manufacturers[13] to contain 2% nitrogen as the only significant impurity, was passed in succession through sodium hydroxide solution, ferrous sulfate–sulfuric acid solution, water and a dense cotton plug.

Solutions.—Solutions were made up by weight to avoid contact with soft glass (ordinary calibrated) volumetric containers, using such precautions that the error in the concentration of the solutions was probably less than 0.01%. In most cases, at least one dilution of each solution was made. Analyses of the diluted solutions showed a maximum error of 0.1%, always in the direction of greater concentration, which is ascribed to evaporation during handling. Purified nitrous oxide was passed into the solutions through a quartz delivery tube.

Solutions more acid than 0.05 *M* were stored in quartz, and the more dilute in non-sol bottles, which were proved satisfactory for the purpose.

Apparatus and Experimental Procedure

The apparatus and method were similar to those used by Brönsted and his students[4,14] with some changes in design and procedure. The solution was shaken in a flask of about 200 ml. capacity and the rate of shaking was adjusted to the resonance period to give maximum agitation; for the same reason the flask was half filled with solution. The flask was closed by a ground glass stopper with a mercury seal. By regrinding the surfaces with levigated alumina and rubbing with Acheson graphite (99.9%), the ungreased joint held a vacuum of less than 1 mm. for several weeks.

The spiral connecting the flask to the manometer system was 3-mm. o. d. Pyrex tubing bent to permit a 2–3 cm. horizontal displacement of the flask. The manometer capillary, made of 1 mm. i. d. tubing, was not graduated itself, since Pyrex cannot be etched accurately, but was surrounded by a soft glass jacket, graduated from 0 to 18 cm. in 0.1 with a maximum error of 0.01 cm. The space between the jacket and the manometer tube was filled with very dilute hydrochloric acid to magnify the meniscus, the acid keeping the glass bright. The mercury reservoir was 5 cm. in diameter so that the maximum movement of the mercury in the manometer produced a fall in level in the reservoir of 0.01 cm. A mercury lubricant composed of dibutyl phthalate saturated with mercury-*p*-ditolyl[15] prevented sticking of the mercury column. The manometer and a very small part of the adjacent gas space were the only portions of the apparatus not immersed. No distillation into this space was observed at any time.

The space over the mercury column was evacuated to the lowest pressure possible with a Hy-Vac pump, because an appreciable pressure in this space would have necessitated a correction for change of room temperature during the run. No leakage into this space occurred over a period of months.

After introduction of the solution, the system was evacuated for two minutes while shaking, then carbon dioxide-free air admitted through a soda lime tower to the flask, the charge of nitramide (approximately 130 mg. = 0.002 mol.) added and the evacuation repeated. The procedure of double evacuation was followed, so that the entire system could be checked before the nitramide was introduced, and to ensure complete removal of the carbon dioxide. After five minutes of the second evacuation, the stopcock to the pump was closed and readings of pressure taken at ten-minute intervals.

In the absence of pretreatment with nitrous oxide, it was found that one to two hours were necessary before the readings could be used, probably due to the expulsion of dissolved air and traces of carbon dioxide by the nitrous oxide being formed. Using solutions containing nitrous oxide reduced this period to twenty or thirty minutes.

Occasionally the manometer temperature during the end-point reading or during the second set of readings (Guggenheim method) was sufficiently different to necessitate a correction for the expansion of the mercury, which never exceeded 0.01 cm. The Beckmann thermometer was compared with a platinum resistance thermometer calibrated by the Bureau of Standards, and with a *verre dur* thermometer calibrated by the International Bureau of Weights and Measures. The temperature of the thermostat[16] was controlled to within 0.01°. During the summer months artificial cooling was obtained by an electric fan directed on the surface of the bath and thrown into circuit on the cooling cycle, by means of a four pole Mercoid switch mounted on the relay of the regulator.

Calculations and Precision

The decomposition follows accurately the unimolecular law

$$k = (1/t) \ln (C_0/C) \qquad (1)$$

The final pressure measures the initial concentration of nitramide C_0. Since

$$C \sim (p_\infty - p);\ \ln (p_\infty - p) = \text{Const.} - kt \qquad (2)$$

or

$$\log (p_\infty - p) = \text{Const.}^* - k^*t \qquad (3)$$
$$\text{where } k^* = 0.4343k$$

Duplicate experiments under various conditions showed that this equation applies accurately. They also indicate that large indeterminate errors, such as effect of dissolved glass, etc., were absent.

Methods of Calculation.—In equation (3) the error in p_∞ exerts a greater influence than do the errors in the various p's. Guggenheim[17] avoids this source of error by taking two complete series of readings, separated by a constant time. However, the Guggenheim method need only be

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[12] Bonner and Wallace, This Journal, **52**, 1747 (1930).

[13] S. S. White Dental Manufacturing Company.

[14] Brönsted and King, This Journal, **47**, 2523 (1925).

[15] Hickman, *J. Opt. Soc. Am.*, **19**, 190 (1929).

[16] Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

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

used when the end-point reading is known with no more, or even less, accuracy than the other readings. In the present experiments, the end-point reading was observed over a long period of time (two to three hours), the reading being sometimes repeated on successive days; consequently it was more precise than any other observation. In check experiments the two methods gave the same results and the same deviation in k; consequently the one chosen for any particular experiment was dictated by convenience.

Guggenheim[17] suggests plotting log $(p'-p)$ against t, where p' refers to the reading in the second set corresponding to the reading p in the first set of observations. However, as Birge[18] has pointed out, graphical methods "give no objective criterion for the error. . . .They are never as accurate as an analytic method, and have no unique solution. . . .One of the most fundamental rules of computing is that the error introduced by the calculation itself shall be negligibly small, compared to the probable experimental error. A graphical solution obviously fails to satisfy this criterion." Although a direct plot and deviation line may be used as directed by Goodwin,[19] this involves considerable work with no certainty that the best solution has been obtained, unless several deviation plots are made.

An especially simple analytic method, if the observations are separated by equal time intervals, has been suggested by Roeser.[20] Applying this method to equation (3)

Let r = log $(p_\infty - p)$
m = number of values of r
i = interval between successive values of r (10 min.)

$$\text{Therefore } k^* = \frac{6}{im(m+1)\,(m-1)}\,\Sigma \qquad (4)$$

where $\Sigma = (m-1)\,(r_m - r_1) + (m-3)\,(r_{m-1} - r_2) + \ldots$

This method is based on the principles of least squares, where all the values r are of equal weight. It is of striking mathematical simplicity in contrast to other schemes.[21]

Errors.—In the construction of the apparatus and calculation of results, the following sources of errors received consideration: (1) assumptions in equation (2) leading to non-linearity of relationship between pressure change and concentration—(a) deviations from Henry's law; (b) deviation from Boyle's law; (c) change in volume of the gas space due to movement of mercury into manometer; (2) errors of apparatus and measurement—(a) non-uniformity of manometer bore; (b) temperature of manometer; (c) error in reading pressure; (d) supersaturation; (e) timing; (f) temperature of thermostat; (3) concentration of the solutions; (4) equality of the weights of the different points r.

Nitrous oxide[22] follows Henry's law in aqueous solution within the error of measurement, which was 0.25%. The assumption that this is the maximum deviation from Henry's law leads to only 0.07% error in equation (2) for the present apparatus. The error increases with increasing ratio of liquid to gas space and equals (3.9 + 6.7 $V_g/V_1)^{-1}$%. In the present case this ratio was 1.5. Nitrous oxide deviates from Boyle's law but in the low pressure range pV is a linear function of the pressure. This corrects equation (2) to

$$C \sim (p_\infty - p)/[1 - A(p_\infty + p)] \qquad (5)$$

where A = 0.0055/atm. at 25°.[23] The maximum correction amounted to 0.07% $(r_m - r_1)$ and was smaller for the succeeding terms of the series Σ.

On correction for error 1 c, eq. (2) becomes

$$C \sim (p_\infty - p)\,[1 + (p_\infty + p - p_1)\pi D^2/4V_g] \qquad (6)$$

where p_1 is first reading used in the calculation and D is diameter of manometer capillary. The maximum correction was 0.04% $(r_m - r_1)$ and was smaller for the succeeding terms of the series Σ

Errors 2a, b and c produced a probable effect of 0.02 cm. This resulted in an error of about 0.5% $(r_m - r_1)$ which was about the same for all the terms of the series Σ. The error changed but slightly with the individual values of r, ranging from *ca.* 0.2% for r_1, to *ca.* 0.3% for r_m.

Pedersen[24] has shown that supersaturation merely invalidates the early readings; after a sufficient induction period, the usual graph of log $(p_\infty - p)$ has the same slope as though supersaturation were absent, provided the rate of stirring is kept constant. Experiments showed the maximum induction period to be four minutes. Error 2d is not present.

Error 2e was 0.02%, the maximum deviation of the watch from a frequency controlled standard. Error 2f amounted to 0.12% of k, based on E_{act} equal to 190 × 10^2 cal. Even at the highest concentration of salt used (2.9 M sodium chloride), error 3 was less than 0.1% k.

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[18] Birge, *Phys. Rev. Suppl.*, **1**, 1 (1929).

[19] Goodwin, "Precision of Measurements and Graphical Methods," McGraw-Hill Book Co., Inc., New York City, 1920.

[20] Roeser, *Bur. Standards Bull.*, **16**, 363 (1920), (Sci. paper 388).

[21] Reed and Theriault, *J. Phys. Chem.*, **35**, 673, 950 (1931).

[22] Findlay and Howell, *J. Chem. Soc.*, **105**, 291 (1914).

[23] Cawood and Patterson, *ibid.*, 619 (1933).

[24] Pedersen, This Journal, **49**, 2681 (1927).

The various errors discussed above have different effects on the weights of the various r's. However, the only significant error is in the measurement of pressure and it has about the same effect on the various r's, the range being 0.2–0.3%. Therefore, all the points have about the same weight, justifying the above application of the method of least squares (*cf.* Roseveare[25] and Luten[26]).

Precision of the Data.—Since the various errors are present to the same extent in all experiments the deviation from the mean can be obtained by an analysis of the results of a large set of duplicate experiments. The results are given in Table I for 0.01 M hydrochloric acid (k^* is given in min.$^{-1}$, M in mole/kg. and C in mole/liter).

TABLE I

Expt.	$k^*_{\text{obs.}}$	Wt.	d
95	0.001187	16	0.000051
97	1243	13	5
144	1239	10	1
148	1234	14	4
189	1249	14	11
191	1235	11	3
220	1233	20	5
222	1236	18	2

Discarding the first value, the weighted mean is 0.001238, the weighted a. d. is 0.000005 and the % d. is 0.4; the maximum variation of the individual values is 1.3%. In 0.5 M hydrochloric acid a greater variation (2.2%) was obtained: $k^* = 0.001251$; a. d. $= 0.000009$; % d. $= 0.7$; $n = 7$ (number of duplicate experiments). Since this a. d. was the largest observed, the diameters of the circles in Figs. 1 and 2 were chosen equal to $0.000009/\sqrt{n}$. In averaging experiments the rate constants were given weights equal to the number of observations used for their calculation.

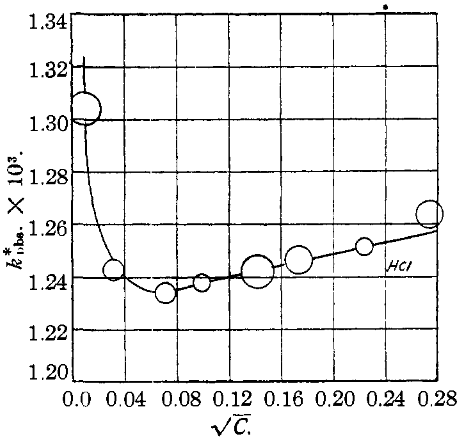

Fig. 1.

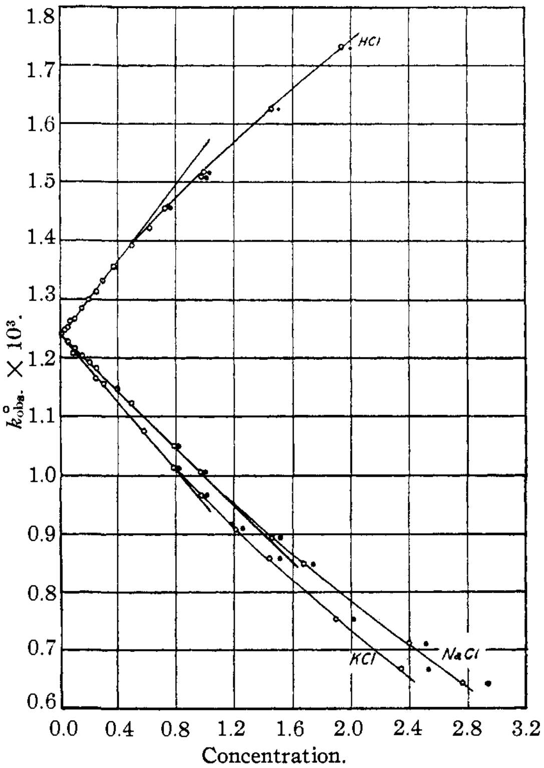

Fig. 2.—Above 0.7 molar: ○, molarity; ●, molality.

After adoption of the precision technique, only 9 values of k in some 180 were rejected and in *all* cases the rejected k's were *lower* than the means of their duplicates, which would be the case if there were a slight leak into the apparatus during the experiment. Since two stopcocks had to be turned to start any experiment and since the apparatus was under vacuum during the entire time (six days in some cases) the occasional occurrence of slight leaks is not surprising. The value of k is sensitive to leaks, as the deviation from the mean of the rejected experiment (No. 95) on 0.01 molal hydrochloric acid can be accounted for by the admission of sufficient air to increase p_∞ by 0.15 cm.

Suggested Improvements in Design.—1. Lengthened manometer tube. This will decrease the effect of the most important error—measurement of pressure. 2. Elimination of all stopcocks in the gas phase. 3. Immersion of the manometer into the thermostat to obviate correction for its temperature change. 4. Decrease of the gas to liquid ratio to enable the use of

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[25] Roseveare, THIS JOURNAL, **53**, 1651 (1931).

[26] Luten, *J. Phys. Chem.*, **39**, 199 (1935).

smaller charges of nitramide, thus compensating for the lengthened manometer tube, which would require larger charges of nitramide.

Data

A typical experiment is given in Table II.

TABLE II

EXPT. No. 191, HCl 0.01000 M, $p_\infty = 15.47$

t	p	$p_\infty - p$	Log $(p_\infty - p)$	k^*
10	4.59	11.18	1.0484	0.00122
20	4.60	10.87	1.0362	121
30	4.90	10.57	1.0241	121
40	5.19	10.28	1.0120	124
50	5.48	9.99	0.9996	124
60	5.76	9.71	.9872	122
70	6.03	9.44	.9750	122
80	6.29	9.18	.9628	124
90	6.55	8.92	.9504	124
100	6.80	8.67	.9380	122
110	7.04	8.43	.9258	125
120	7.28	8.19	.9133	124
130	7.51	7.96	.9009	122
140	7.73	7.74	.8887	125
150	7.95	7.52	.8762	123
160	8.16	7.31	.8639	126
170	8.37	7.10	.8513	

The graph of $\log(p_\infty - p)$ *vs.* t is a straight line after the forty minutes reading with slope 0.001239.

Using readings 40 to 170: $m = 14$, $i = 10$, $\Sigma = 5.6179$, $k^*_{\text{obs.}} = 0.001235$ min.$^{-1}$.

TABLE III

HYDROCHLORIC ACID SOLUTIONS

n	M	C	$k^*_{\text{obs.}}$	C_W	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_W C_W$
2	0.0000100	0.0000100	Drift	55.35	...
2	.0001000	.0000997	1.304×10^{-3}	55.35	...
5	.001000	.000997	1.243	55.34	...
5	.00500	.00499	1.234	55.34	...
7	.01000	.00997	1.238	55.33	0.004×10^{-3}
2	.01999	.01993	1.242	55.31	.008
3	.03000	.02990	1.246	55.29	.012
7	.05000	.04981	1.251	55.24	.018
3	.07499	.07467	1.263	55.20	.031
2	.1000	.09953	1.267	55.14	.037
2	.1500	.1492	1.285	55.04	.057
4	.2000	.1987	1.298	54.94	.072
2	.2500	.2481	1.314	54.84	.090
2	.2997	.2972	1.331	54.75	.109
2	.3750	.3713	1.356	54.59	.138
3	.5000	.4940	1.391	54.34	.178
2	.6248	.6158	1.422	54.09	.215
1	.7449	.7325	1.455	53.85	.253
2	.7493	.7368	1.456	53.84	.254
2	1.0000	.9787	1.510	53.34	.320
3	1.0202	.9981	1.517	53.30	.328
5	1.5000	1.4542	1.625	52.36	.457
3	2.0000	1.9294	1.730	51.35	.584

The results of sets of experiments at various concentrations are given in Tables III, IV, V and VI. The densities required for the conversion from molality to molarity were taken from "International Critical Tables"[27] or calculated by the rule of mixtures which has been shown to hold for aqueous solutions of hydrochloric acid, sodium chloride and potassium chloride.[28]

In the hydrochloric acid solutions (Fig. 1) the velocity constant reaches a minimum between 0.001 and 0.005 M. The square root of the concentration has been used to magnify the scale at very low concentrations. The values for the extremely dilute acid solution (10^{-5} M hydrochloric acid) drifted continuously during the course of the experiments from an initial value of 0.0013 to 0.0015 when half completed, the average value being about 10% greater than that for 0.01 M hydrochloric acid, which is identical with the 10% increase found by Brönsted and King[5] for the velocity of decomposition in "pure water" over that in "acid" solution at 15°. However, their claim that the deviations from the unimolecular course were not measurable if the observations were confined to the first two-thirds of the reaction was not confirmed, due we believe to the greater precision of our measurements.

The observed k^*'s of Tables III, IV, and V at concentrations greater than 0.005 M are plotted in Fig. 2 against both molarity and molality, the differences being greater than the experimental error above 0.7 molar. For simplicity the curves connecting the molality values have not been drawn. Similarly, to avoid confusion, points and curves of $k^*_{\text{obs.}}$ *vs.* mole fraction have not been added; they lie between the molarity and molality points but nearer the molarity values. It appears that for this reaction a linear relation holds to a slightly higher concentration for the molarity scale.

The velocity constant may be considered as composite: $k = k_0 + k_s C_s$ (7) where k_0 = spontaneous velocity constant (water reaction), k_s = velocity constant for S (acid or salt), and C_s = concentration of S. Extrapolating the hydrochloric acid curve to zero concentration

$$k^*_0 = 1.235 \times 10^{-3}$$

The limiting slopes in Fig. 2 and the concentrations over which they are valid

$k^*_{\text{HCl, obs.}} = +\,0.328 \times 10^{-3}$ from 0 to 0.4 molar
$k^*_{\text{NaCl, obs.}} = -\,0.245 \times 10^{-3}$ from 0 to 1.0 molar
$k^*_{\text{KCl, obs.}} = -\,0.291 \times 10^{-3}$ from 0 to 0.8 molar

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(27) "International Critical Tables," Vol. III, pp. 54, 79, 87.

(28) Ruby and Kawai, THIS JOURNAL, **48**, 1119 (1926).

TABLE IV

SODIUM CHLORIDE SOLUTIONS, $M_{\text{HCl}} = 0.01000$

n	M_{NaCl}	C_{NaCl}	$C_{\text{H}_3\text{OCl}}$	$k^*_{\text{obs.}}$	C_W	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_W C_W - k^*_{\text{H}_3\text{OCl}} C_{\text{H}_3\text{OCl}}$
2	0.05035	0.05015	0.00996	1.227 × 10^{-3}	55.28	−0.010 × 10^{-3}
1	.1005	.0999	.00995	1.216	55.23	− .020
2	.1512	.1503	.00994	1.204	55.18	− .031
2	.2005	.1991	.00994	1.193	55.13	− .041
2	.2471	.2452	.00993	1.183	55.08	− .050
1	.4010	.3969	.00991	1.148	54.93	− .081
2	.4947	.4889	.00988	1.124	54.84	− .103
2	.8020	.7880	.00983	1.050	54.53	− .170
2	.9887	.9680	.00979	1.005	54.23	− .209
2	1.504	1.458	.00969	0.892	53.80	− .312
2	1.733	1.672	.00965	.848	53.56	− .350
3	2.506	2.381	.00950	.711	52.74	− .469
3	2.927	2.758	.00942	.643	52.28	− .527

TABLE V

POTASSIUM CHLORIDE SOLUTIONS, $M_{\text{HCl}} = 0.01000$

n	M_{KCl}	C_{KCl}	$C_{\text{H}_3\text{OCl}}$	$k^*_{\text{obs.}}$	C_w	$k^*_{\text{corr.}} = k^*_{\text{obs.}} - k^*_w C_w - k^*_{\text{H}_3\text{OCl}} \text{H}_3\text{OCl}$
3	0.04006	0.03989	0.00996	1.228 × 10^{-3}	55.27	−0.009 × 10^{-3}
3	.09004	.08955	.00995	1.210	55.19	− .025
3	.1502	.1491	.00993	1.200	55.10	− .033
3	.2455	.2431	.00990	1.166	54.95	− .064
2	.3000	.2966	.00989	1.156	54.87	− .072
2	.5881	.5768	.00981	1.076	54.42	− .142
3	.8024	.7821	.00975	1.012	54.09	− .199
3	1.0031	.9721	.00969	0.966	53.78	− .238
3	1.252	1.205	.00962	.907	53.39	− .288
3	1.502	1.435	.00955	.857	53.00	− .329
2	2.009	1.890	.00941	.752	52.21	− .417
2	2.521	2.337	.00927	.668	51.44	− .483

TABLE VI

HYDROCHLORIC ACID–POTASSIUM CHLORIDE SOLUTIONS

n	M_{HCl}	M_{KCl}	C_{HCl}	C_{KCl}	$k^*_{\text{obs.}}$
2	0.0000100	0.0000101	0.0000100	0.0000101	Drift
2	.0001000	.0001008	.0000997	.0001005	1.283 × 10^{-3}
2	.001000	.001008	.000997	.001005	1.239
2	.004961	.004963	.004946	.004948	1.230
2	.05000	.05002	.04974	.04976	1.237
2	.1250	.3752	.1231	.3694	1.160
2	.1500	.1501	.1485	.1486	1.240
2	.2999	.1000	.2966	.09889	1.281
2	.3750	.3761	.3674	.3685	1.232
2	.5000	.2501	.4905	.2453	1.299
1	.5000	.5005	.4870	.4874	1.228
2	.7449	.2556	.7272	.2495	1.346
2	1.0000	.5040	.9646	.4861	1.316
3	0.9999	1.0003	.9590	.9594	1.176
5	1.4997	0.5001	1.4347	.4784	1.436

Water Correction

k_0 is the velocity constant due to the catalysis by water and equals $k_w C_w$. At 24.84° the molar catalytic constant for water is $k^*_w = 0.02231 \times 10^{-3}$. For high concentrations of acid and salt it cannot be assumed that C_w has a constant value of 55.51 m./l. Accordingly, equation (7) is more properly written $k = k_w C_w + k_s C_s$ and correction should be made for the reduced concentration of water as acid and salt are added. Furthermore, in the hydrochloric acid solutions, the proton exists as H_3O^+, still further decreasing the water concentration. Accordingly

$k_{\text{corr.}} = k_{\text{obs.}} - k_w C_w$ for the HCl solutions
$k_{\text{corr.}} = k_{\text{obs.}} - k_w C_w - k_{\text{H}_3\text{OCl}} C_{\text{H}_3\text{OCl}}$ for the NaCl and KCl in 0.01 *M* HCl solutions

The recalculated results are given in the last columns of Tables III, IV and V; the corrected *k*'s have been plotted against the molarities. The limiting slopes and the concentrations over which they are valid

$k^*_{\text{H}_3\text{OCl, corr.}} = +\,0.367 \times 10^{-3}$ from 0 to 0.4 molar
$k^*_{\text{NaCl, corr.}} = -\,0.213 \times 10^{-3}$ from 0 to 1.4 molar
$k^*_{\text{KCl, corr.}} = -\,0.251 \times 10^{-3}$ from 0 to 0.8 molar

Miscellaneous Experiments

Heavy Water.—Some experiments were conducted with a solution of heavy water containing 4.72 mole per cent. of D_2O (d_{25} 1.00213 g./ml.). To ensure proper purification, a specimen of ordinary water purposely contaminated with potassium hydroxide, rubber and laboratory sweepings was purified at the same time and concurrent experiments carried out with both specimens. In the distillations the liquids were heated to dryness in the stills and the sprayhead and condenser flamed to remove the last traces of water, which was necessary to avoid waste and isotopic separation during the purification. The receivers were kept in freezing mixtures during the distillations. The samples were redistilled five times at atmospheric pressure from various purifying agents and finally in a special two-flask apparatus by vaporization *in vacuo*. The vacuum was broken with purified nitrous oxide and the distillates poured into tared non-sol bottles. By means of a micro weighing buret, a few drops of constant boiling hydrochloric acid was added to make the solutions 0.01 *M* in hydrochloric acid. After one experiment, without withdrawing the solution, an additional charge of nitramide was added and a second experiment carried out. Then the proper amount of potassium chloride was added to make the solutions 1 *M* in potassium chloride and two more experiments performed. The results are given in Table VII.

TABLE VII

Solution	Expt.	$k^*_{\text{obs.}}$	Wt.	Mean
0.00982 *M* HCl in 4.72% D_2O	181	1.174×10^{-3}	35	1.176×10^{-3}
	183	1.178	29	
0.00976 *M* HCl in H_2O	182	1.246	35	1.249
	184	1.252	29	
0.00982 *M* HCl + 1.000 *M* KCl in 4.72% D_2O	185	0.923	29	0.919
	187	.915	26	
0.00976 *M* HCl + 1.000 *M* KCl in H_2O	186	.976	29	0.971
	188	.966	26	

It is evident that the method of purification was adequate. The mean for the 0.01 *M* HCl in H_2O is 0.9% higher, and the mean for the 0.01 *M* HCl + 1 *M* KCl in H_2O is but 0.4% higher than those for the corresponding solutions made up by the usual method.

The velocity constant for 0.01 *M* HCl in 4.7% D_2O is 5.8% lower, and the velocity constant for 0.01 *M* HCl + 1 *M* KCl in 4.7% D_2O is 5.2% lower than those for the corresponding H_2O solutions. An investigation of this striking result is in progress.

Mercuric Chloride.—While studying the effect on the reaction velocity of all possible substances in the system, mercury, mercurous chloride and mercuric chloride were tried. The first two had no effect, but the last showed a marked positive catalysis. In 0.01 *M* HCl + *ca.* 10^{-5} *M* $HgCl_2$, k^* was 2×10^{-3}, an increase of 75% over that in the same solution without the mercuric chloride. This effect is probably related to the molecular rather than ionic nature of mercuric chloride in solution and merits further investigation.

Discussion

Comparison with Previous Work.—Contrary to the earlier published findings from Brönsted's laboratory, a marked primary salt effect and an appreciable acid catalysis were found. On communication of these results, Professor Brönsted disclosed the following values of the velocity constant[29] obtained at 15° in potassium chloride solutions containing a little hydrochloric acid.

C_{KCl}, m./l.	1.00	1.50	2.00
k^*	31.85	27.90	24.50×10^{-5}

They show the same negative salt effects reported here.

After this study was initiated in 1929, Brönsted and Vance[7] reported an acid catalysis in isoamyl alcohol. The molar catalytic constant found was approximately the same for both hydrochloric and hydrobromic acids, which they ascribe to the ion $C_5H_{11}OH_2^+$. For 0.1 *M* this acid effect was about 100 times larger than the spontaneous reaction. Brönsted and his students have not found an acid catalysis in aqueous solution due to the restricted acid range in which they worked, the lower precision of their measurements and the relatively small magnitude of the effect.

Salt Effect.—The action of added salt on the decomposition of nitramide is undoubtedly a primary salt effect upon the catalysis by water. The effect is large amounting to an 18% decrease for 1 molar sodium chloride and 22% for 1 molar potassium chloride.

Of the reactions subject to generalized base catalysis, only one other, the enolization of acetoacetic ethyl ester, has been studied in concentrated salt solutions. For the spontaneous reaction in water Pedersen[30] has found a large linear negative salt effect amounting to 18% in 1 molar sodium chloride and 22% in 1 molar potassium chloride at 18°. This exact agreement with the nitramide results, which can hardly be fortuitous since the temperature effect is very small, points to the same cause operating in the two cases, which is the effect of the salts on the basic proper-

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[29] Brönsted, private communication; experiments made in 1926–27.

[30] Pedersen, *J. Phys. Chem.*, **37**, 751 (1933).

ties of water. (The acid catalysis by water of both reactions must be vanishingly small compared to the base catalysis.) This salt effect is probably due to hydration, since thereby water is removed. Indeed, it is even possible to calculate the average hydration of the ions required to produce the decrease, the values obtained being similar to those given by other methods.

Using Brönsted's results at 15° and the corresponding values at 24.84° interpolated from the curve in Fig. 2, the constants in the integrated form of the Arrhenius equation, $\log k^* = B - E/2.3026RT$ are

C_{KCl}, m./l.	1.00	1.50	2.00
B	10.90	10.71	10.72
E	189.8	187.6	188.9 × 10² cal.

The minor variation is within the precision of the data.

Acid Effect.—The positive effect of hydrochloric acid on the decomposition of nitramide is small, being of the same order of magnitude as the salt effects. The increase in reaction velocity is only 2.6% in 0.1 molar hydrochloric acid. Pedersen found a similar increase (3.8%) for the enolization of acetoacetic ethyl ester and was uncertain as to whether it represented primary salt effect or hydrogen ion catalysis. For the nitramide reaction there is little doubt that the effect is acid catalysis, because of the existence of acid catalysis in isoamyl alcohol.[7] The much smaller value of the acid catalysis in water is to be expected from the leveling effect of the base water on strong acids.

Another and better proof of acid catalysis is given by Fig. 3, in which $\log k^*_{\text{corr.}}$ for the hydrochloric acid effect is plotted against the acidity function, $H_0 = -\log a_{\text{H}^+}(f_{\text{B}}/f_{\text{BH}^+})$, using for the latter the values of Hammett and Paul.[31] With the exception of the value in 2 *M* hydrochloric acid, all the points agree with the straight line within the experimental error. (The error is large for the first two points because $k^*_{\text{corr.}}$ is obtained as the difference of two quantities which are almost equal.)

Although there may also be a primary salt effect of the hydrochloric acid on the water catalysis, it must be quite small because it is extremely unlikely, as Fig. 3 shows, that this salt effect would follow the same mathematical relationship as the acid catalysis.

Mechanism of the Decomposition.—Pedersen[32] has suggested a plausible mechanism for the decomposition by bases. He assumes that the following equilibria are attained practically instantaneously

$$H_2N{\cdot}NO_2 \rightleftarrows HN{=}NO_2^- + H^+ \rightleftarrows HN{=}NOOH$$

and that there is present at all times a constant, but very small, fraction of the undissociated nitramide in the form HN=NOOH. He explains the decomposition as taking place when bases remove the last proton bound to the nitrogen. Since HN=NOOH is a neutral molecule, this explanation is in conformity with the absence of appreciable salt effect in dilute solution, as found by Brönsted and his students for all their experiments no matter what the charge type of the base. It should be pointed out that the assumption of a very small fraction of the undissociated nitramide present as HN=NOOH is not necessary, since the decomposition can just as well be explained by assuming that *all* the undissociated nitramide is present in this form and that a very *small* percentage of the collisions by bases is fruitful. Indeed Hantzsch[33] maintains that the nitramide ordinarily exists in the form HN=NOOH rather than $H_2N{\cdot}NO_2$.

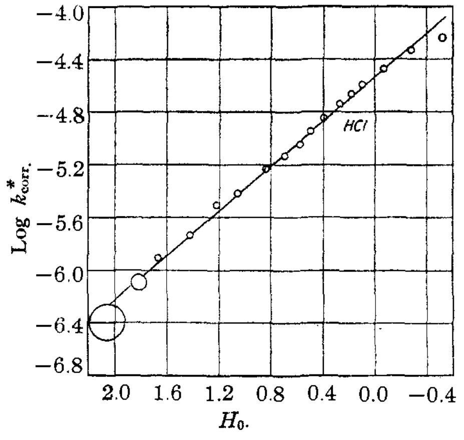

Fig. 3.

It is difficult to see why Pedersen accepts the mechanism proposed by Brönsted to explain the rise in reaction velocity in solutions of very low acidity (pure water). Brönsted postulated[6] that the nitramide ion decomposes about twenty times more rapidly than the undissociated nitramide, so that the increased dissociation as the acidity is decreased causes a more rapid decom-

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[31] Hammett and Paul, THIS JOURNAL, **56**, 827 (1934).

[32] Pedersen, *J. Phys. Chem.*, **38**, 581 (1934). *Vide*, p. 589.

[33] Hantzsch, *Ber.*, **66B**, 1566 (1933).

position. However, the results are just as well explained by assuming catalysis of the undissociated nitramide by OH^-, which increases in concentration as the acidity is decreased. Brönsted mentioned this possibility in an earlier paper.[5] Indeed, because of the equilibrium

$$H_2N_2O_2 + OH^- \rightleftharpoons HN_2O_2^- + H_2O$$

it is impossible to differentiate kinetically between the two such conceptions. However, equivalence of the interpretation is not a sufficient reason for a departure from the first mechanism of the nitramide decomposition as a basic catalysis of the molecule.

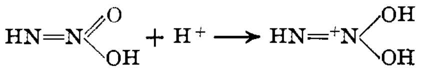
Assuming catalysis of the molecule by OH^-, the molar velocity constant was calculated from the measurements made below 0.005 *M* HCl, in which range the velocity constant increases (see Fig. 1). In calculating the OH^- concentration, correction was made for the influence of the nitramide present for which the dissociation constant of nitramide was taken to be 2.55×10^{-7}, the value for 15°.[5] The results are given in Table VIII.

TABLE VIII

C_{HCl}	C_{OH^-}	$k^*_{obs.}$	$(k^*_{obs.} - k^*_{0,\ corr.})/C_{OH^-}$
0.001000	1×10^{-11}	1.243×10^{-3}	$0.8 \times 10^{+6}$
.0001000	0.8×10^{-10}	1.304	$0.9 \times 10^{+6}$
.0000100	0.2×10^{-9}	*ca.* 1.45	*ca.* $1.1 \times 10^{+6}$

The agreement is within the precision of the data. This molar velocity constant is about 2000 times the most rapid hitherto measured for the nitramide decomposition. A very long and probably unjustified extrapolation of the Brönsted and Pedersen formula[2b] indicates about 10^9 for k_{OH^-} at 15°.

We advance the following mechanism to explain the acid catalysis



$$HN{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix} + H^+ \longrightarrow HN{=}^+N\begin{smallmatrix}\nearrow OH\\ \searrow OH\end{smallmatrix}$$

The substance formed should be unstable, since two OH groups have never been known to be bound to one nitrogen atom, and therefore the compound should decompose into nitrous oxide and oxonium ion.

Acknowledgment is made to the College of the City of New York for the use of some of the apparatus for this investigation.

Summary and Conclusions

1. The preparation and the measurement of the decomposition of nitramide was studied to render this desirable reaction more conveniently available for kinetic investigations.
2. An improved method of preparation of nitramide is outlined.
3. The rate of decomposition of nitramide has been measured in aqueous acid and salt solutions over a wide range of concentrations with an error of about 1%.
4. A detailed analysis of the errors has been presented.
5. Suggestions have been advanced for an improved apparatus, so as to make the measurement of the velocity of a chemical reaction proceeding by gas evolution more precise.
6. A negative primary salt effect has been found which is ascribed to the effect of salt on the catalytic properties of the base water. The constants of the Arrhenius equation have been calculated.
7. An acid catalysis has been found which is closely correlated with the acidity function H_0.
8. Pedersen's mechanism for the basic catalysis has been discussed and simplified. The catalytic constant for hydroxyl ion is about 2000 times greater than that of any other base measured previously.
9. A mechanism for the acid catalysis has been advanced.
10. Heavy water decreases the velocity of the decomposition as compared to ordinary water.
11. Mercuric chloride has a marked positive effect on the reaction velocity.

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