acetyl radicals. No evidence on these points is available, although the data of Anderson and Rollefson[4] rather tend to disprove such an assumption. The decrease in carbon monoxide yield at low pressures is probably not sufficient to lend support to this hypothesis, although perhaps data at still lower pressures would be necessary to prove the point.

The reaction

$$CH_3 + CH_3CO = C_2H_6 + CO \quad (4)$$

suggested by Gorin[3] is not very plausible from a theoretical standpoint, although kinetic studies do not offer very definite evidence one way or the other in this connection.

In conclusion it may be stated that the work herein presented supports the conclusion, previously drawn,[2] that the reaction leading to biacetyl and the reaction leading to carbon monoxide are both largely homogeneous at high intensities. Thus we agree with Anderson and Rollefson that the reactions are either both homogeneous or both heterogeneous under these conditions. At low intensities, however, we find support for the conclusion that the reaction leading to biacetyl is largely a wall reaction and the reaction leading to carbon monoxide (apart from the primary process) is largely a homogeneous gas phase reaction. The picture of acetone decomposition is quite consistent and satisfactory, although it is unfortunate that quantitative expressions embodying all of the steps become so complicated that they cannot be applied to the data.

Summary

1. At low intensities the addition of large amounts of carbon dioxide to acetone causes an increase in the quantum yield of carbon monoxide formation from the latter.

2. It is pointed out that the data agree with the mechanism previously presented in which the reaction leading to carbon monoxide formation is a homogeneous gas phase decomposition of the acetyl radical. Part of the carbon monoxide is also formed during the primary process. The reaction leading to biacetyl seems to be largely a wall reaction at low intensities and to become increasingly a homogeneous gas phase reaction at high intensities and also at high pressures.

Rochester, New York Received August 18, 1941

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

The Base Catalyzed Decomposition of Nitramide in Aqueous Solution

By L. K. J. Tong and A. R. Olson

The first systematic study of the decomposition of nitramide $H_2N_2O_2$, into nitrous oxide and water was reported by Brønsted and Pedersen,[1] who showed that the decomposition was catalyzed by the ions of weak acids, the weaker the acid the greater the effect. As a result of this study they enunciated their theory of generalized acid and base catalysis. Thus the base catalyzed reaction was expressed by the equation

$$k_c K^{\nu} = G \quad (1)$$

where k_c is the rate of the reaction, K is the dissociation constant of the acid, G is a constant, and ν is a continuous function of K which varies from 0 for very weak acids, to 1 for very strong acids. This expression they derived by making the following assumptions: (1) if HA is a stronger acid than HB, then the specific rate of dissociation of HA is greater than that for HB and in addition, the specific rate of association of H^+ and A^- is less than the corresponding rate for H^+ and B^-. (2) The catalysis by a base is of the same character as its association reaction with hydrogen ion, and so the specific catalytic rate is proportional to the rate of association. (3) In the region of very weak acids the association reaction approaches the limit where every collision is effective and so the base catalyzed reaction also must approach a limit. The variation in K in this region is due almost entirely to a variation in the rate of dissociation. The first assumption requires that ν be less than unity, the third, that it approach zero in the strong base region. The variation in ν introduces a curvature in the plot of log k vs. log K. In the nitramide decomposition, ν was found to be a constant. This Brønsted and Pedersen attributed to the fact that the catalysts which they employed did not differ sufficiently in base strength.

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[1] Brønsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); see also Brønsted, *Chem. Rev.*, **5**, 231 (1928).

As one phase of a more extended investigation, we have measured the rate of nitramide decomposition using stronger basic ions than Brønsted and Pedersen employed, paying particular attention to competing reactions.

Procedure

The apparatus was a gas manometer connected to a reaction flask by a flexible glass coil, as described by Brønsted and Duus.[2] The volume of the solution used in each run was 25 cc. and the gaseous volume of the system was 190 cc. In order to eliminate carbon dioxide from the solution, the reaction flask was rinsed with nitrogen, and then the solution was introduced rapidly with a pipet. The position of the apparatus in the thermostat made it convenient initially to have about fifteen centimeters of gas pressure in the apparatus, and so, after the system had been assembled, it was evacuated and then the solution was saturated with nitrous oxide while the flask was being shaken. This process of evacuation and saturation was repeated twice in order to displace the air by nitrous oxide, for preliminary experiments showed that if a large quantity of air were present, the final readings drifted due to slow diffusion. In making a run, the zero time was taken as the instant the nitramide was dropped into the solution.

Preparation of Materials

Nitramide.—The method of preparation described by Thiele and Lachman[3] was used, followed by the modified process of extraction given by Marlies and LaMer.[4] The product was purified by precipitation several times from ether solution by adding pentane, and finally by subliming it in a high vacuum at 40° and condensing it on glass surface cooled by liquid air. From pressure changes it was found to yield over 99% nitrous oxide. The titration of a barium hydroxide solution in which some nitramide had been decomposed, showed no strong acid or basic impurity.

2,4-Dichlorophenol, *o*-nitrophenol and 2,4-dinitrophenol were Eastman Kodak Co. products. The first was recrystallized from water and the last two were recrystallized several times from water–alcohol mixtures.

Phenol was first dried by adding "Drierite" at a temperature slightly above the melting point of phenol. The dried liquid was decanted into a small flask and distilled. The colorless crystals were kept in a desiccator over calcium chloride.

Barium hydroxide solutions were prepared by diluting a stock solution made by dissolving C. P. barium hydroxide in sufficient water to make the final concentration approximately 0.1 *N*. After allowing the solution to stand for several days, the clear supernatant solution was siphoned into another bottle previously rinsed with nitrogen. This solution was kept free of carbon dioxide by means of a soda lime tube. The concentration was determined by titrating against standardized hydrochloric acid.

Phenolate and substituted phenolate solutions were prepared by partially neutralizing the acids with standardized sodium hydroxide (or when necessary, by barium hydroxide) and diluting to the proper volume by adding carbon dioxide free water.

Cyanide Solution.—A stock solution of potassium cyanide was prepared by dissolving enough "Baker's Analyzed" 96% potassium cyanide in water to produce a 0.5 *M* solution. To each liter of this solution 24 g. of barium nitrate was added to precipitate carbonate impurities. When a solvent containing hydrocyanic acid was required, it was prepared from the above solution by partially neutralizing it with standardized hydrochloric acid. The stock solution was analyzed by Liebig's method for cyanides and by titrating it with hydrochloric acid using methyl red indicator.

Experimental

Nitramide is a weak acid and so when it is added to a solution of a basic ion, the following equilibrium is established

$$\mathrm{HN} + \mathrm{B}^- \rightleftarrows \mathrm{N}^- + \mathrm{HB}$$

where HN and N^- denote nitramide and its ion, respectively. The stronger the base, the more completely will it be neutralized and if the nitramide is in excess, the more nearly will (N^-) equal the original (B^-). As the limiting experiment in this direction we added nitramide to solutions of barium hydroxide.[5]

Several runs were made in which we varied the initial concentrations of barium hydroxide, keeping the total initial concentration of nitramide constant at about 0.1 *M*. Invariably, the initial rate of decomposition was slow. Toward the end of the run, the rate suddenly became immeasurably fast, as shown in Curve I, Fig. 1. In every run, the change occurred at the time when the excess nitramide had disappeared. Further change therefore was at the expense of nitramide ion which must have produced hydroxide ion. Setting the total rate of disappearance of nitramide equal to the sum of all the probable partial rates, we obtain

$$-\frac{1}{2.3}\frac{d(\mathrm{HN})}{dt} = k_1(\mathrm{HN}) + k_2(\mathrm{HN})(\mathrm{N}^-) + k_3(\mathrm{N}^-) + k_4(\mathrm{N}^-)(\mathrm{OH}^-) + k_5(\mathrm{HN})(\mathrm{OH}^-) \quad (2)$$

where each of these concentrations at any time before the rapid change occurred can be determined from the equilibrium constants, the initial conditions and the pressure of nitrous oxide. We thus see that in the earlier portion of the run, (N^-) is essentially constant, and that (OH^-) is so small that the term $k_4(N^-)(OH^-)$ can be neglected since k_4, as shown in a later section, is not extremely large. Furthermore, $k_3(N^-)$ and $k_5(HN)(OH^-)$ are kinetically indistinguishable for

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

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

[4] Marlies and LaMer, THIS JOURNAL, **57**, 2008 (1935).

[5] Brønsted and King, *ibid.*, **49**, 193 (1927), used solutions of this type in their conductivity measurements.

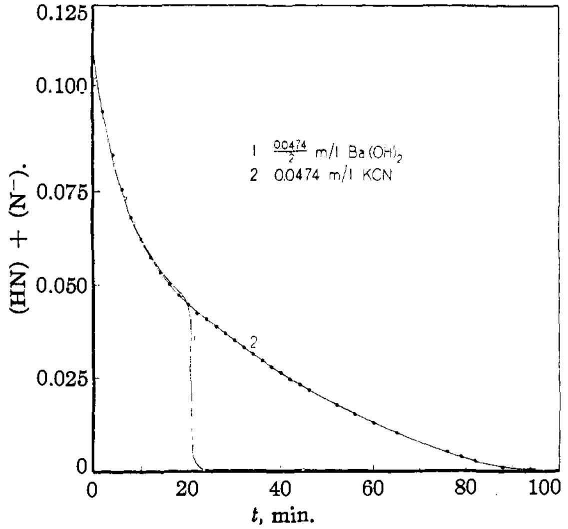

Fig. 1.

the latter term is equal to $k_5(K_W/K_{HN})(N^-)$. Equation (2) reduces, therefore, to

$$-\frac{1}{2.3}\frac{d(HN)}{dt} = k_1(HN) + k_2(HN)(N^-) + k_3'(N^-)$$

which we can write as

$$-\frac{1}{2.3}\frac{d(HN)}{dt} = [k_1 + k_2(N^-)]\left[(HN) + \frac{k_3'(N^-)}{k_1 + k_2(N^-)}\right]$$

or since (N^-) is approximately constant

$$-\frac{1}{2.3}\frac{d(HN)}{dt} = A[(HN) + B/A]$$

and finally

$$\frac{d \ln [(HN) + B/A]}{2.3dt} = -A \qquad (2')$$

where $A = k_1 + k_2(N^-)$, and

$$B = \left[k_3 + k_5\frac{K_W}{K_{HN}}\right](N^-) = k_3'(N^-)$$

Equation (2′) corresponds to a first order decomposition of nitramide using the fictitious concentration $[C(t) - D]$, where $C(t)$ is the sum of the concentration of nitramide and its ion at time t and D is an empirical constant which can be determined by graphing log $[C(t) - x)]$ against time; the particular value of x which makes the graph a straight line is D. The slope of the line is $-A$. D is related to other quantities by the equation $D = (N^-) - B/A$ which permits a valuation of B. Using Marlies and LaMer's[6] value for k_1 (*i. e.*, 1.24×10^{-3}), we obtain k_2 and k_3' as shown in Table I. k_2 agrees well with the value obtained by Brønsted and Pedersen when allowance is made for the temperature difference between the two investigations.

TABLE I

Run no.	(N^-)	A	k_2	k_3'
1	0.485×10^{-2}	0.607×10^{-2}	0.99	8.2×10^{-3}
2	2.06×10^{-2}	2.10×10^{-2}	.96	8.5×10^{-3}
3	2.57×10^{-2}	2.58×10^{-2}	.96	9.5×10^{-3}
4	4.74×10^{-2}	4.60×10^{-2}	.95	9.6×10^{-3}
		Weighted av.	.96	9.0×10^{-3}

With other basic catalysts, in addition to the rates discussed above, we must consider the catalytic decomposition of nitramide by B^-, and also the reaction between HB and N^-. However, since these are kinetically indistinguishable, we shall assume that the latter does not occur, thus giving the maximum value to the rate of the former reaction. In addition, if the base is strong enough, it will be hydrolyzed; and so we also might have to consider the catalytic decomposition of N^- by hydroxide ion. As an example of the former class, we have investigated the decomposition of nitramide in solutions of *o*-nitrophenolate.

The velocity of the reaction can be expressed as

$$-\frac{d(HN)}{2.3\,dt} = k_1(HN) + k_2(HN)(N^-) + k_3'(N^-) + k_7'(B^-)(HN) \qquad (3)$$

where B^- denotes the *o*-nitrophenolate ion. This equation can be handled by the method in the preceding section. Thus let the initial concentration of (HB) $= a$ and that of $(B^-) = b$ and add to the solution such a quantity of nitramide so that if no reaction occurred its concentration would be c. As long as $c(t)/(a + b)$ is large enough, and K_{HB}/K_{HN} is small enough for the reaction $HN + B^- \rightarrow HB + N^-$ to be almost complete, the following approximations will be valid

$$(N^-) \cong b$$
$$(HN) = c - (N^-) \cong a - b$$
$$(HB) = c + (N^-) \cong a + b$$
$$(B^-)(HN) \cong (K_{HB}/K_{HN})b(a + b)$$

On substituting into equation (3) and reducing as before, we obtain

$$-d \log [(HN) + B/A]/dt = A$$

where

$$A = k_1 + k_2 b$$

and

$$B = [k_3' + k_7'(K_{HB}/K_{HN})(a + b)]b$$

This equation can be used to determine k_7' as soon as K_{HN} and K_{HB} are known.

The dissociation constant of *o*-nitrophenol was found by Holleman to be 6.8×10^{-8}.[7] We de-

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[6] Marlies and LaMer, THIS JOURNAL, **57**, 1812 (1935).

[7] Holleman, *Rec. trav. chim.*, **21**, 432 (1902).

termined the ionization constant of nitramide in the following manner: *o*-nitrophenolate ion has an intense yellow color whereas *o*-nitrophenol is only slightly colored. Colorimetric measurements were made on an aqueous solution in which the total concentration of *o*-nitrophenol and its ion was kept constant but the relative amount of the two was varied by adding hydrochloric acid in order to calibrate the instrument in terms of the concentration of these two substances. Then to the solution containing the same amounts of phenol and phenolate as above, a known quantity of nitramide was added. Measurements again were taken and repeated at short intervals for about half an hour. Approximately four minutes lapsed between the time of mixing and the time of the first reading. On extrapolating the colorimetric readings to zero time, we obtained the concentrations of all substances in solution and thus sufficient data to calculate K_{HN}. In Table II we have listed these concentrations for four different determinations.

TABLE II

Expt.	(B^-)	(HB)	(N^-)	(HN)	K_{HN}/K_{HB}
1	2×10^{-4}	74×10^{-4}	8.3×10^{-4}	65×10^{-4}	4.73
2	3.56	74	6.7	28.3	4.92
3	4.15	50.3	6.2	15.6	4.82
4	5.00	51.8	5.3	11.1	4.95
				Av.	4.85

K_{HN} is thus found to be 3.3×10^{-7} at 25° which is consistent with the value of 2.57×10^{-7} which Brønsted and King obtained from conductivity measurements at 15°. Since the ratio of the two constants is about five, it is necessary that the concentration of HN be considerably greater than that of the *o*-nitrophenol in order to render the above approximations valid; in our experiments this ratio was initially about twenty to one.

Instead of pursuing this analytical method any further, we can combine our pressure measurements with a graphical method for calculating our constants. Thus from the pressure and the equilibrium constants we can calculate the equilibrium concentrations of nitramide, nitramide ion, *o*-nitrophenol and *o*-nitrophenolate ion. These, together with the specific rate constants k_1, k_2 and k_3' which we found in the preceding section, enable us to calculate the rate of production of nitrous oxide by three of the paths mentioned above. For a particular run, these rates are plotted as functions of time as shown on curves 1, 2 and 3 in Fig. 2. The graphical integration of these rates

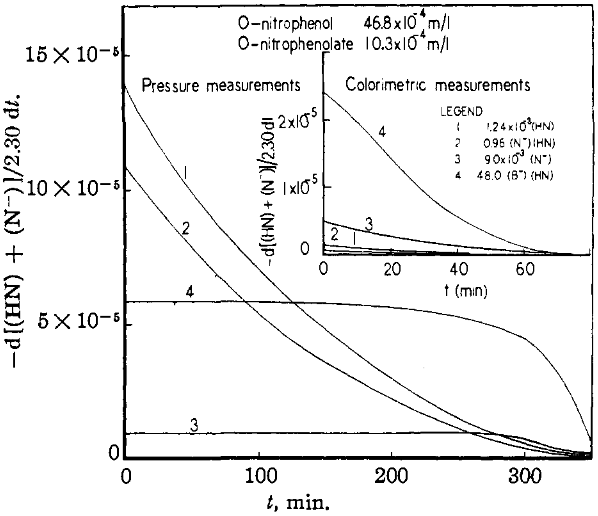

Fig. 2.

corresponds to the pressure changes produced by these paths as shown in curves 1, 2 and 3 in Fig. 3. The difference between the sum of these quantities and the total amount of nitrous oxide, must be due to the catalyzed decomposition of nitramide by B^-. This difference is represented by curve 4 of Fig. 3. Fortunately, the earlier portion of this curve is almost straight which permits an easy evaluation of the specific rate constant. From this the actual rate has been calculated and plotted as curve 4, Fig. 2.

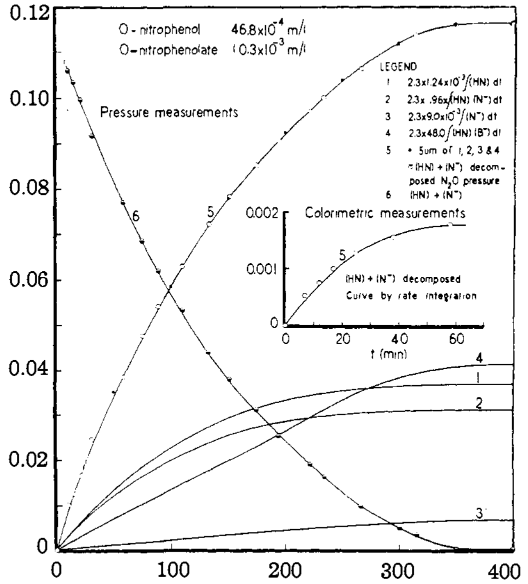

Fig. 3.

We also could follow the total rate of decomposition by colorimetric measurements instead of pressure measurements. The inserts in Figs. 2 and 3 refer to a run followed in this manner where the initial concentration of nitramide is much smaller than that used in the pressure measurements.

When barium phenolate is substituted for barium *o*-nitrophenolate, we again have the reactions discussed in the preceding paragraph. Phenolate ion is, however, hydrolyzed to a sufficiently large extent so that we must consider the rate of the catalyzed decomposition of nitramide ion by hydroxide ion. The amount of hydrolysis depends upon the ratio $(B^-)/(HB)$ and so this reaction assumes importance only toward the end of the run. In the first portion of the run, therefore, the calculations can be handled precisely as before. The difference between curves 1 and 2 in Fig. 4 shows the discrepancy between the calculated and the observed results, which must be due to the hydroxide ion reaction. The product of the calculated values of (N^-) and (OH^-) times a constant is shown in the insert of Fig. 4 as a function of time. The area under this curve to some time, *t*, must be equal to the difference between curves 1 and 2. That factor of proportionality gives immediately the specific rate constant, *i. e.*, 2.7×10^8.

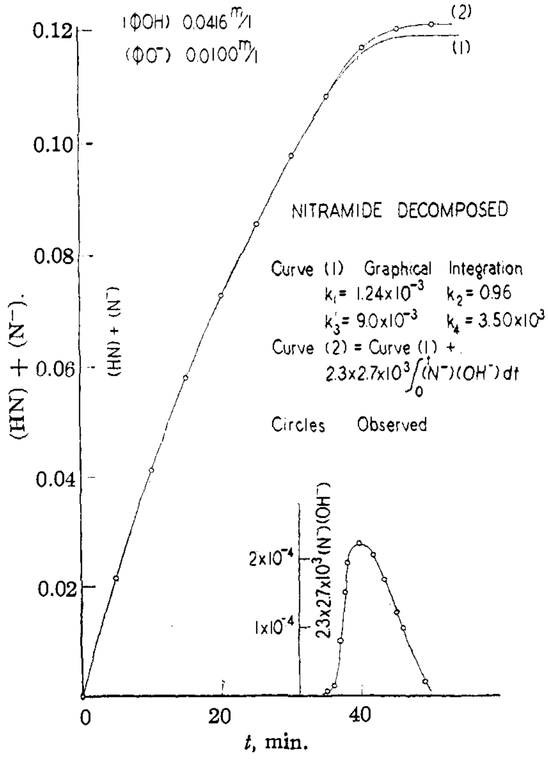

Fig. 4.

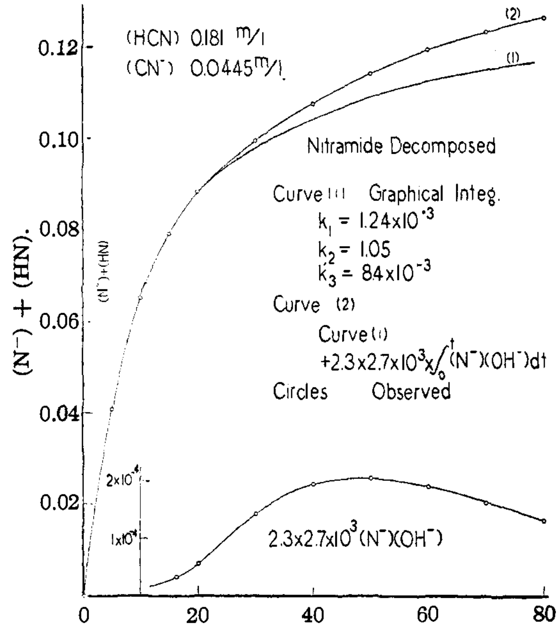

Fig. 5.

In Fig. 5 we have shown the corresponding measurements and calculations for cyanide ion. Surprisingly enough, if cyanide ion shows any catalytic behavior it is less than the error of the experiment. This may seem peculiar when we can give a definite value to the catalytic constant of catalysts like dinitrophenolate ion, which is so much smaller than the upper limit assigned to cyanide ion. However it must be remembered that we do not determine k_{B^-} directly but $k_{B^-}(K_{HB}/K_{HN})$. The amount of nitramide ion decomposed by hydroxide ion becomes more important not because (OH^-) is large but because catalysis by cyanide ion is absent. It should be noted that the specific rate, k_2, has increased by 10%. This increase was found only in those runs which contained a large excess of hydrocyanic acid.[8] The constant given above for the hydroxide and nitramide ion reaction accounts for the rapid change in barium hydroxide solutions toward the end of the run as shown in Fig. 1.

In Table III we have collected the rate constants from this investigation, and in Fig. 6 we have plotted them in the conventional way (log *k vs.* log K_b) together with some of the data published by Baughan and Bell.[9] No corrections have been made for statistical factors, since the introduction of such factors will not make mate-

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(8) This appears to be due to some catalytic effect of the non-ionized acid.

(9) Baughan and Bell, *Proc. Roy. Soc.* (London), **158**, 464 (1937).

TABLE III

Base	K_a	Acid, *a*	Salt, *b*	*k*	Method of calcn.
Hydroxide[a]	1.8×10^{-16}			$3 \pm 0.3 \times 10^5$	Analytical
Phenolate	1.3×10^{-10}	0.0416	0.0100	3.5×10^3	Graph
				3.49×10^3	Analyt.
		.0109	.0100	3.47×10^3	Analyt.
		.103	.0100	3.60×10^3	Analyt.
				3.62×10^3	Graph
		.082	.050	3.4×10^3	Init. slope
		.0532	.0236	3.38×10^3	Analyt.
2,4-Dichlorophenolate	1.8×10^{-8}	.037[b]	.00100	226	Analyt.
		.0005	.0118	227	Analyt.
o-Nitrophenolate	6.8×10^{-8}	.00468	.00103	48	Graph
				46	Colorimetric, Graphical
2,4-Dinitrophenolate	8.13×10^{-5}	Satd.	.050	0.344	First order rate equation
Benzoate	6.61×10^{-5}	Satd.	.00	.626	
		Satd.	.040	.620	
Cyanide	7.2×10^{-10}	0.181	.0445	>3	Analyt.
Nitramide ion[a]	3.3×10^{-7}			0.96	Analyt.

[a] See Table I. [b] Saturated solution.

rial changes, neither have any corrections been made for salt effects since these also are small.

The low catalytic activity of nitramide ion led Brønsted and Pedersen to believe that it might be a pseudo acid. If a similar explanation is offered for the failure of cyanide ion to fall on the curve, we would have to postulate that hydrocyanic acid is ten thousand times as strong as it generally is assumed to be.

It was pointed out in the section concerning barium hydroxide solutions that the rate of spontaneous decomposition of nitramide ion and the rate of decomposition of nitramide catalyzed by hydroxide ion are kinetically indistinguishable. The most likely assumption is that some goes by each path, *i. e.*, that when we set $k_3' = k_3 + k_5 \cdot (K_W/K_{HN})$ neither k_3 nor k_5 is zero. In making Table III we have set $k_3 = 0$, thus giving a maximum value to k_5. A corresponding assumption is implied in all the other catalytic coefficients. Thus the two rates $k_6(\mathrm{HB})(\mathrm{N}^-)$ and $k_7(\mathrm{HN})(\mathrm{B}^-)$ are indistinguishable, for the latter term can be written $k_7'(K_{HB}/K_{HN})(\mathrm{HB})(\mathrm{N}^-)$. The assumption therefore is that k_6 is zero.

Baughan and Bell found that the rates for each catalyst such as acetate ion obey an Arrhenius equation. Nevertheless, when they extrapolated to obtain a rate for the acid $K_b = 1$, they found that the rates for such an acid do not obey an Arrhenius equation. It should be noted that their extrapolation was done by taking the best straight line through their data. Figure 6 shows that the extrapolations should be done by means of curves. This curvature, small though it is at this point, may be sufficient to account for this discrepancy.

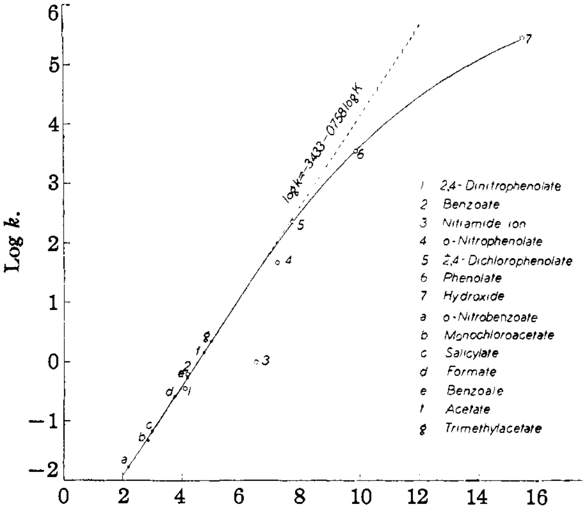

Fig. 6.

Summary

The decomposition of nitramide in aqueous solutions containing ions of very weak acids has been investigated.

When the logarithms of the specific rates of catalysis are graphed against the logarithm of the basic constants of the catalysts, a curve such as that postulated in the original work by Brønsted and Pedersen is obtained.

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