6. Values of the salting-out constant, *Ks*, have been estimated for different mixtures of potassium dihydrogen phosphate and dipotassium phosphate.

7. Tables and graphs are given which facilitate the preparation of buffer solutions of the same ionic strength and varying *P*H or of the same *P*H and varying ionic strength.

BOSTON, MASSACHUSETTS

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

# THE DISSOCIATION CONSTANT OF NITRAMIDE

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RECEIVED NOVEMBER 18, 1926 PUBLISHED JANUARY 11, 1927

## 1. Introduction

In a kinetic study of the decomposition of nitramide into nitrous oxide and water,[1] $H_2N_2O_2 \longrightarrow N_2O + H_2O$, it was found that the reaction under ordinary conditions is divisible into two partial reactions, one of which is catalytic and the other "spontaneous" in nature. In sufficiently acid solution containing only strong acids, the spontaneous decomposition is the only measurable reaction independent of the concentration of the acid. In 0.01 and 0.001 *N* hydrochloric acid, for example, the velocities are practically identical. If the acidity is considerably lower the velocity increases, which may be due either to a spontaneous reaction of the nitramide anion, $HN_2O_2^- \longrightarrow N_2O + OH^-$, or to the catalytic effect of hydroxyl ions increasing in number as the acidity decreases.

For an exact interpretation of the phenomena of the catalytic and spontaneous decomposition of nitramide in solutions of small acidity—phenomena which are the subject of further study in this Laboratory—it would be valuable to know with some accuracy to what extent nitramide dissociates under the prevailing conditions. For that purpose we have carried out the present investigation to determine the dissociation constant of nitramide as an acid.

Immediately after the discovery of nitramide by Thiele and Lachman[2] in 1895, there arose some discussion on the strength of the compound as an acid. While Thiele and Lachman themselves, from consideration of the chemical properties of the substance, thought it a rather strong acid, Hantzsch and Kaufmann[3] concluded from conductivity measurements that it was only very weakly dissociated. They did not find it possible

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[1] (a) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924). (b) Brönsted and Duus, *ibid.*, **117**, 299 (1925).

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

[3] Hantzsch and Kaufmann, *Ann.*, **292**, 317 (1896).

to calculate its dissociation constant on the basis of their measurements, but Hantzsch concluded[4] that the new compound was about 500 times weaker than acetic acid.

Baur[5] pointed out that the measurements of Hantzsch and Kaufmann are apparently wrong, in that the equivalent conductance decreases with decreasing concentration, and he carried out a series of measurements at 0° in order to diminish the decomposition of the nitramide during the measurements. The equivalent conductances found by him are given in Table I, $v$ denoting the molar volume.

TABLE I

BAUR'S DATA FOR THE EQUIVALENT CONDUCTIVITY OF NITRAMIDE

| $v$ | 1.941 | 1.977 | 8.052 | 14.580 | 26.760 | 63.105 |
|---|---|---|---|---|---|---|
| $\Lambda$ | 0.520 | 0.538 | 0.600 | 0.702 | 0.848 | 1.126 |

These values are considerably lower than those of Hantzsch and Kaufmann. Baur found it impossible to get the conductance of the sodium salt of the nitramide, which would be necessary for computing $\Lambda$ at infinite dilution. With any reasonable value for $\Lambda$, however, the data of Baur—as Hantzsch pointed out—lead to values for $K$ which are far from being constant when the concentration changes.

On the basis of our experiments, one source of error in these conductivity measurements is evident. Baur states that in 15 minutes the conductivity for $v$ = 63.11 fell from 1.126 to 1.042. This corresponds to a percentage decomposition of the nitramide in 15 minutes that, according to our measurements, would normally take over three hours at 15° and presumably about six hours at 0°. It occurred to us that this enormous acceleration might be due to the influence of the platinized electrodes in the conductivity cell presumably used in Baur's determinations. This effect of platinized platinum was completely verified by some velocity measurements made by the method of determining the pressure of the nitrous oxide evolved as described in previous papers,[1] and it was found at the same time that bright platinum does not have such an effect, at least to an extent measurable under ordinary conditions.

The rapid decomposition in the presence of platinum black not only changes the total concentration of the nitramide, but also causes inexactness and fluctuation in the readings unless the solution be vigorously stirred. We found it necessary, therefore, to reëxamine the conductivity of nitramide solutions, using bright platinum electrodes. These conditions permit a fairly accurate measurement of the conductivity of the free nitramide, and also the values for the sodium salt (even though this probably cannot be made in the solid state) proved to be quite easily obtainable.

[4] Hantzsch, *Ann.*, **292,** 340 (1896).

[5] Baur, *Ann.*, **296,** 95 (1897).

## 2. Method of Procedure

While the instability of a substance usually interferes more or less with accurate determinations of its properties, we are able, in this determination of the dissociation constant of the free nitramide, to take advantage of the slow decomposition of the substance to simplify the experimental procedure. Since in the decomposition of nitramide only nitrous oxide and water are formed, neither of which has any influence upon the conductivity of the solution, the result of the decomposition, as far as the conductivity measurements are concerned, is simply a continuous decrease in concentration of the weak acid. We need not make up, therefore, as many solutions as we are going to measure, but only the strongest of them, thus obtaining by slow decomposition the more dilute.

In order thus to utilize the spontaneous decrease in concentration, it is of course necessary to know exactly the rate of decomposition of nitramide dissolved in pure water. According to the previous investigations the spontaneous decomposition at 15° is given by $\log c_0/c = 0.00038\, t$, where log denotes decadic logarithms and $t$ is measured in minutes.

As already stated, the velocity of decomposition increases somewhat when the acidity decreases. For nitramide dissolved in pure water we found, by the method described in previous publications,[6] in two experiments, 0.000417 and 0.000421 for the unimolecular velocity constant; thus, as an average $k = 0.000419$, which is 10% higher than in "acid" solution. Actually we should not expect a strictly unimolecular reaction when pure water is used as solvent, since the acidity of the solution changes during the reaction; however, using for the calculations only the first two-thirds of the reaction, deviations from the unimolecular course are not measurable. From the equation $\log c_0/c = 0.000419\, t$, thus obtained for the decomposition in pure water solution, the concentration $c$ of the nitramide solution in the conductivity cell could be calculated at any time desired, when the concentration $c_0$ is known from the amount of nitramide originally taken.

For the determination of the conductivity of the sodium salt of nitramide, $NaHN_2O_2$, the conductivity cell was first charged with a dil. sodium hydroxide solution and then an excess of nitramide added, neutralizing the base and causing a corresponding drop in the conductivity of the solution. The solution contains then the sodium salt and some free nitramide, the conductivity of which can be neglected since the acid in the presence of its sodium salt is practically undissociated. For the same reason the decomposition of the nitramide going on in the solution does not at the beginning alter the conductivity because it leaves the concentration of the salt unchanged. Readings can thus be made with ease in the solution during this period of decomposition. When, however, all the excess

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[6] Brönsted and King, THIS JOURNAL, 47, 2523 (1925); Ref. 1.

of nitramide has disappeared, the alkalinity of the solution suddenly increases strongly, this in turn accelerating the rate of decomposition of the anion of nitramide, $HN_2O_2^- \longrightarrow N_2O + OH^-$, so that in a few minutes the solution of the sodium salt has changed over completely to a solution of sodium hydroxide present in the same concentration as at the start of the experiment. Therefore, following the drop in conductance, on addition of the nitramide to the base we have to expect, first, a period of constant conductivity and then after some time a rapid increase to the original value. This expectation was completely verified by the experiments.

The nitramide is a sufficiently weak acid to allow the application of the classical dissociation and conductivity laws to the solutions employed. In the case of the nitramide salt, which dissociates completely, the classical laws are not well applicable, but it is possible to extrapolate with sufficient accuracy to great dilution and thus determine the conductivity of the nitramide ion. The method also presupposes that the conductivities of hydrogen ion and sodium ion at the same concentration and temperature are known.

## 3. Experimental Part

Nitramide was prepared as described elsewhere[7] and recrystallized by dissolving in pure ether and precipitating by addition of chloroform to the solution. The white, flaky crystals were filtered on a cotton plug in a funnel, dried by sucking dry, dust-free air through them. The substance was stored in a desiccator over sulfuric acid, in a cool place.

It was attempted to purify a sample further by repeating the recrystallization, but with no improvement, as evidenced by the fact that the conductance of a solution of equal concentration was no lower. It was also attempted to purify further some of the material by sublimation in a vacuum, condensing the sublimed product on a surface cooled by carbon dioxide snow. This method also led to no improvement of the product.

The conductance of the various solutions was measured with a Kohlrausch circular slide-wire bridge and resistance coil box, telephone and an induction coil as the source of current. This type of outfit gave conductances sufficiently accurate for the purpose desired. The conductance of the sodium salt was measured in a cell having platinized electrodes; as already mentioned, it was found impossible to use platinized electrodes with the solutions of nitramide itself, as decomposition was greatly accelerated. For instance, in one experiment the conductance of a solution fell to 0.7 of its original value, showing that the nitramide was half decomposed in less than one hour, whereas with no acceleration the time of half decomposition would have been about 13 hours. Consequently, for these solutions a similar cell with bright platinum electrodes was used. Undoubtedly the decomposition in the case of the nitramide salt is also

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[7] Ref. 2, p. 297.

accelerated by black platinum electrodes, but this reaction does not affect the conductivity in the constant period.

All solutions were made up in ordinary distilled water having a specific conductance of 1.2 to 1.4 × $10^{-6}$ mhos. If this conductance is due mainly to dissolved carbon dioxide[8] it can easily be shown that even with the most dilute solutions of nitramide used for the calculations, the conductance due to this dissolved carbon dioxide would be less than 1% of the whole, and so it was not considered necessary to prepare purer water. As for the sodium salt solutions, the sodium hydroxide solution used in making them was free from carbonate, and air free from carbon dioxide was bubbled for some time through the water used for their preparation. Suitable precautions were taken to prevent access of carbon dioxide from the air to the solutions while making them up and measuring their conductance.

For determinations of the conductivity of the free nitramide, 50 cc. of water was placed in the cell, and when it had come to the temperature of the bath (15 ± 0.01°) sufficient nitramide to make the solution 0.03 *M* (that is, 0.0935 g.) was dropped in; nitrogen was bubbled in to stir the solution until the crystals were dissolved and the solution thoroughly mixed, and then the resistance was measured as quickly as possible. Then at suitable intervals of time, readings were made again. The results of a typical experiment are given in Table II.

TABLE II

MEASURED CONDUCTANCE OF PURE NITRAMIDE SOLUTIONS AT 15° IN A TYPICAL EXPERIMENT

$CH_2N_2O_2$ at start = 0.03 *M*. Cell constant = 0.04874

| Time, hrs. | 2 (min.) | 1 | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|---|---|
| Sp. cond. × $10^5$ | 3.05 | 2.99 | 2.88 | 2.80 | 2.71 | 2.63 | 2.58 | 2.40 |
| Time, hrs. | 13 | 23 | 26 | 30 | 47 | 49 | 71 | |
| Sp. cond. × $10^5$ | 2.11 | 1.59 | 1.46 | 1.29 | 0.788 | 0.727 | 0.340 | |

The measurements of several such experiments were plotted and values read from the smooth curve to use in the final calculations. By means of the equation $\log c_0/c = -kt$ where, according to the measurements mentioned above, $k = 0.000419$ and $c_0 = 0.03$, the concentration of nitramide corresponding to the time of the conductivity readings during the course of the experiment, was calculated. The concentrations $c$ and equivalent conductances $\Lambda$ so obtained are given in Table V.

Without making use of the value for the conductivity at infinite dilution necessary for the final determination of the degree of dissociation, the conductivity data thus obtained furnish an excellent proof of their reliability and real significance in the fact that they lead to exactly the same rate of

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[8] Kendall, THIS JOURNAL, 39, 7 (1917).

decomposition as the method already mentioned above. Due to the weakness of nitramide as an acid, the mass-action law requires that the total concentration of the substance vary proportionally to the square of the conductivity. In fact, plotting log $\Lambda^2$ as ordinate against time (in minutes) as abscissa an exactly straight line is obtained having the slope $\Delta \log \Lambda^2/\Delta$ time = 0.000417, in complete agreement with the value 0.000419 of the first method. The different conductivity values are, therefore, in agreement with the mass-action law, which again is tantamount to stating that the measurements at the different concentrations of nitramide actually lead to a constant value for the dissociation constant.

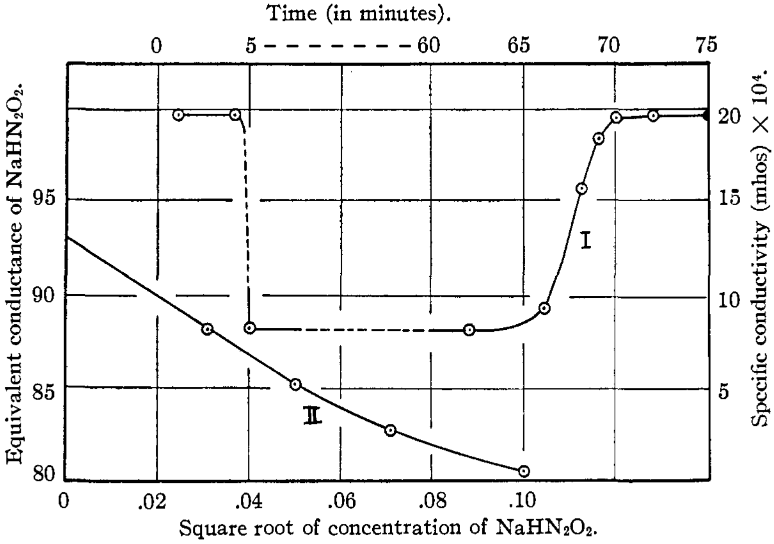

Fig. 1.

The conductances of solutions of the sodium salt were measured in the following way. One hundred and fifty cc. of sodium hydroxide solution of suitable concentration was placed in the cell—with the necessary precautions—and its resistance measured, whereafter an excess of nitramide was introduced and dissolved. The conductance of the solution then showed the characteristic course already mentioned in Part 2, first falling to that of the sodium salt and remaining constant there for some time while the excess of nitramide was slowly decomposing. As soon as the solution became appreciably alkaline, the remaining nitramide decomposed very rapidly and the conductance rose at once to that of the sodium hydroxide solution again. This behavior is shown clearly in Curve I of Fig. 1, which gives the details of a typical experiment. That an excess of nitramide does not change the conductance of the salt, and that its conductance is negligible in comparison with that of the salt, is shown by the fact that the conductance remains absolutely constant as long as a sufficient excess of nitramide is present, although its concentration is changing continually.

The results of five determinations with different salt concentration are given in Table III.

TABLE III

MEASURED CONDUCTANCES OF SOLUTIONS OF $NaHN_2O_2$

Cell constant = 0.07048

<table>
<tr><td>$NaHN_2O_2$</td><td>0.01</td><td>0.005</td><td>0.0025</td><td>0.001</td><td>0.001</td></tr>
<tr><td>Sp. cond. × $10^4$</td><td>8.06</td><td>4.14</td><td>2.13</td><td>0.877</td><td>0.885</td></tr>
<tr><td>Λ (equiv. cond.)</td><td>80.6</td><td>82.8</td><td>85.2</td><td>87.7</td><td>88.5</td></tr>
<tr><td></td><td></td><td></td><td></td><td colspan="2">88.1</td></tr>
</table>

## 4. Calculation of the Constant

In order to determine the dissociation constant of nitramide:

$$K = \frac{c_{HN_2O_2^-}\, c_{H^+}}{c_{H_2N_2O_2}} = c\,\frac{\alpha^2}{1-\alpha}$$

where $\alpha = \Lambda/\Lambda_\infty$

it is necessary first to find the value of $\Lambda_\infty$ from our measurements with the sodium salt of nitramide, the data for which are given in Table III. Plotting the Λ values against the square root of the salt concentration[9] the points approach a straight line, from which, as shown in Curve II, Fig. 1, an extrapolation value $\Lambda_\infty = 93$ for the sodium salt in very dilute solution can be obtained. Even if this method does not insure an exact extrapolation it is undoubtedly sufficiently accurate for the present purpose, as $\Lambda_\infty$ enters in such a way that a difference of one or two units makes only a small difference in the value of $K$.

Measurements of the conductance in great dilution of hydrogen and sodium ions at 15° are not available; there are, however, measurements at 25° and 18°, and it was considered sufficiently accurate to make a linear

TABLE IV

EQUIVALENT CONDUCTANCES OF THE SODIUM AND HYDROGEN IONS AT INFINITE DILUTION

| | | | | | | | | Extrapolated values | |
|---|---|---|---|---|---|---|---|---|---|
| Ion | $Na^+$ | $Na^+$ | $Na^+$ | $H^+$ | $H^+$ | $H^+$ | $H^+$ | $Na^+$ | $H^+$ |
| Temp., °C | 18 | 18 | 25 | 18 | 18 | 25 | 25 | 15 | 15 |
| Λ | 43.23 | 43.4 | 51.2 | 314.5 | 313.9 | 350 | 347.2 | 39.9 | 298 |
| Ref. | 10 | 11 | 11 | 11 | 12 | 11 | 13 | | |

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[9] (a) Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," 2nd ed., Leipzig, **1916**, pp. 108, 112. (b) Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

[10] Washburn, THIS JOURNAL, **40**, 158 (1918).

[11] Noyes and Falk, *ibid.*, **34**, 461 (1912).

[12] Kendall, *ibid.*, **101**, 1293 (1912).

[13] Kohlrausch, *Z. Elektrochem.*, **14**, 129 (1908).

extrapolation from these values to 15°. The values are collected in Table IV with the extrapolated values.

Then $\Lambda_\infty H_2N_2O_2 = 298 + 93 - 39.9 = 351.1$.

By means of the $c$ values and $\Lambda$ values of Table IV and the value of $\Lambda_\infty$ thus determined, the degree of dissociation $\alpha$ and finally the dissociation constant $K = c\alpha^2/(1-\alpha)$ is calculated. These values and their average are found in the last line of Table V.

TABLE V

EQUIVALENT CONDUCTIVITY AND IONIZATION CONSTANT OF NITRAMIDE

| | | | | | |
|---|---|---|---|---|---|
| $c$ | 0.03 | 0.015 | 0.0075 | 0.00375 | 0.001875 |
| $\Lambda$ | 1.017 | 1.446 | 2.052 | 2.89 | 4.053 |
| $K$ | $2.52 \times 10^{-7}$ | 2.56 | 2.58 | 2.56 | 2.53 |
| | | | | Av. | $2.55 \times 10^{-7}$ |

The mean value for the dissociation constant at 15° is then $K = 2.55 \times 10^{-7}$, showing nitramide to be an acid about 70 times as weak as acetic acid. The good agreement between the single values also shows—as one would expect—that there is no question of a second step dissociation under the conditions of these experiments.

It should be mentioned finally that some colorimetric measurements with bromothymol blue in dilute buffers of nitramide partially neutralized with sodium hydroxide solution gave about $3 \times 10^{-7}$ for the dissociation constant at room temperature, about 20°, in sufficient agreement with the conductivity measurements.

This work was carried out while the junior author held a fellowship of the American-Scandinavian Foundation, during 1924–1925, and the authors accordingly wish to express their thanks to the Foundation.

## Summary

1. The decomposition of nitramide according to the scheme $H_2N_2O_2 \longrightarrow H_2O + N_2O$ is strongly catalyzed by platinum black, but not affected appreciably by bright platinum.

2. The unimolecular decomposition of nitramide at 15° in dilute pure water solution is 10% faster than the "spontaneous" decomposition in acid solution.

3. The dissociation constant of nitramide as an acid is $K = 2.55 \times 10^{-7}$ at 15°.