# The Decomposition of Nitroacetic Acid in Concentrated Aqueous Solutions of Some Non-Electrolytes

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Nitroacetic acid decomposes in aqueous solution into nitromethane and carbon dioxide. The first kinetical investigations of this reaction were carried out simultaneously by Heuberger [1, 2] and by the author of this paper [3]. The reaction is of the first order when the hydrogen ion concentration is kept constant. Nitroacetic acid is a dibasic acid. Its first dissociation constant is 0.0210 at 18° C and zero ionic strength (this paper and [4]). The second dissociation constant is, according to Heuberger [2], about 10^{-9}. Both the undissociated acid and the divalent ion, $^-OON:CH \cdot COO^-$, are stable, while the univalent ion decomposes spontaneously. The maximum velocity constant is therefore found in solutions where practically all the nitroacetic acid is transformed into the univalent ion, *e. g.* in acetate buffers. In more acid solutions, say in hydrochloric acid, the velocity constant is smaller and proportional to the degree of dissociation of the nitroacetic acid.

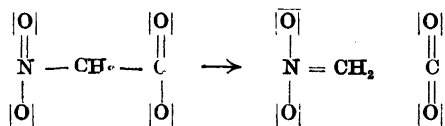There are three possible forms of the univalent nitroacetate ion, namely

$$O_2N \cdot CH_2 \cdot COO^-, \quad HOON:CH \cdot COO^-, \quad and \quad ^-OON:CH \cdot COOH$$
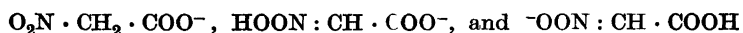
The author of this paper has shown [4] that the first, and probably only the first, of these splits off carbon dioxide directly, and that the primary reaction product is the aci-form of nitromethane. The rate determining step is therefore

$$O_2N \cdot CH_2 \cdot COO^- \longrightarrow {}^-OON:CH_2 + CO_2$$
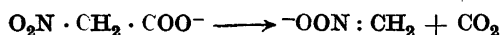
The ion formed takes up a proton, and, finally, the aci-nitromethane rearranges into normal nitromethane. It was suggested as a hypothesis that the decomposition takes place when a valency electron in an activated nitroacetate ion

is displaced from the oxygen atom of the carboxylate group through the mole-
cule to the oxygen atom of the nitro group as illustrated in the following
scheme where a line denotes a pair of electrons

$$\begin{array}{ccccc} |O| & |O| & \overline{|O|} & |O| \\ \| & \| & | & \| \\ N - CH - C & \longrightarrow & N = CH_2 & C \\ | & | & | & \| \\ |O| & |O| & |O| & |O| \end{array}$$

In this paper, the decomposition is examined in aqueous solutions of
dioxane, urea, glucose, and sucrose. In the first part, the velocity constant
for the decomposition of the nitroacetate ion is determined. From a study of
the influence of a gradual exchange of water molecules with those of the non-
electrolyte, we may hope to find out whether water takes a direct part in
the reaction as suggested by Heuberger [2], and whether the rate depends upon
the dielectric constant of the medium. The urea solutions have a higher, the
other solutions studied a lower dielectric constant than pure water. In the
second part of the paper, the dissociation constant of nitroacetic acid is deter-
mined from the velocity constant in solutions containing hydrochloric acid in
addition to the non-electrolyte.

The measurements were carried out at the temperature 18.00° C. The
initial concentration of nitroacetic acid was always about 0.02 molar. The
reaction was followed by observing the pressure above the solution during the
reaction. The experimental procedure was the same as in earlier papers [4, 5].
The nitroacetic acid was prepared in the same way as earlier [3]. It was recryst-
allized twice from chloroform. Two preparations (melting points 92 and 93° C)
were used. They gave concordant results. Dioxane which had been purified
two years earlier [6] was again refluxed with sodium and distilled in an all-
glass apparatus fitted with a column containing glass beads. The freezing
point of the fraction used for the measurements was 11.65° C, while pure dioxane
freezes [7] at 11.80°. The urea was partly a Kahlbaum preparation »for scientific
purposes», partly the same recrystallized twice from alcohol. The two prepara-
tions gave concordant results. The sugars were Merck's purest anhydrous
glucose and a high-grade, large-crystalline cane sugar.

THE VELOCITY CONSTANT FOR THE DECOMPOSITION OF THE NITRO-ACETATE ION

The solutions examined in this part of the paper contain, in addition to the
non-electrolyte, 0.100 molar acetic acid and 0.100 molar sodium acetate. The
ratio between the dissociation constants of nitroacetic acid and acetic acid is,

in dilute aqueous solution, more than 10^3. Owing to the similarity in structure of the two acids, this ratio will probably not change much when going from pure water to the solutions investigated. That this holds for the dioxane solutions, is seen from table 4. We may therefore conclude that the nitroacetic acid, in all the solutions containing the acetate buffer, has been practically completely transformed into the univalent ion.

The results of the measurements are given in table 1. k^* is the velocity constant per minute based on decadic logarithms.

Table 1. The decomposition of nitroacetic acid in aqueous solutions of non-electrolytes at 18.0° C. The solutions contain in addition 0.100 molar acetic acid and 0.100 molar sodium acetate.

Dioxane

Molarity	Molality	Mole fraction	k^*
0.000	0.000	0.00000	0.02482
0.495	0.522	0.00931	0.02661
0.999	1.099	0.01942	0.02864
1.998	2.411	0.04162	0.03450
3.006	4.028	0.06766	0.04327
4.003	6.014	0.09776	0.05578

Urea

Molarity	Molality	Mole fraction	k^*
0.998	1.057	0.0187	0.02672
2.005	2.228	0.0386	0.02890
3.004	3.516	0.0596	0.03145
3.998	4.936	0.0817	0.03392

Glucose

Molarity			k^*
0.500			0.02434
1.000			0.02380
1.500			0.02342
2.000			0.02317

Sucrose

Molarity	Per cent		k^*
0.250	8.27		0.02473
0.500	16.02		0.02453
0.750	23.34		0.02453
1.000	30.21		0.02453
1.250	36.75		0.0244
1.500	42.90		0.0244
2.000	54.35		0.0243

When the sucrose concentration was more than 1 molar, the equilibrium between the carbon dioxide of the solution and the gas phase was not established sufficiently quickly to prevent a supersaturation effect. When log P for these experiments was plotted against the time t (P being the difference between the final pressure reading and the reading at the time t), the points did not, as usually, all fall close to a straight line, but formed a curve which rapidly approached a straight line with increasing t. This effect has been discussed earlier [8]. The velocity constant k^* is here the numerical value of the slope of the straight line approached. Owing to this complication, the velocity constants for solutions containing more than 1 molar sucrose are not quite as accurate as those for the other solutions.

In the experiments on solutions of urea, the pressure did not keep completely constant when all the nitroacetic acid was decomposed, but increased slowly, possibly owing to a slow hydrolysis of urea. This increase was, however, too slow to have any importance for the accuracy of the measurements.

It is seen from table 1 that the velocity constant for the decomposition of the nitroacetate ion increases with increasing concentrations of dioxane and urea, while it decreases a little when glucose is added. Sucrose has almost no effect. Even when more than half of the water has been replaced by sucrose, the decrease of k^* is only 2 per cent. These results show that the decomposition does not necessarily proceed *via* a chemical reaction with a water molecule.

The measurements show no dependence between the velocity of decomposition and the dielectric constant (ε) of the medium. In the dioxane solutions examined, ε decreases [9] from 81 to 50, in the urea solutions it increases [10] to about 88, while in both cases k^* increases. In the sucrose solutions, k^* is nearly constant, while ε decreases [11] from 81 to about 45. In the glucose solutions, k^* decreases slightly, while ε decreases [11] from 81 to about 40.

In fig. 1, the open circles show k^* for urea solutions plotted against the mole fraction (N_U) of urea. The points fall close to a straight line of which the equation is

$$k^* = 0.02482 + 0.110 \, N_U$$

The solid circles represent k^* for dioxane solutions plotted against the mole fraction of dioxane. Here a curved line is obtained. If we, however, plot against the mole fraction $N_D{}'$ of a hypothetical tetrahydrate of dioxane (crossed circles), the relation is again linear. It is represented by the equation

$$k^* = 0.02482 + 0.1940 \, N_D{}'$$

It is uncertain whether this result has any real significance. In favour of the assumption that a hydrate of dioxane is formed speak the following facts. A

Fig. 1. The velocity constant k* for the decomposition of the nitroacetate ion at 18° C. (1) in solutions of dioxane, plotted against the mole fraction of dioxane (I), and against the mole fraction of dioxane tetrahydrate (II); (2) in solutions of urea, plotted against the mole fraction of urea (III).
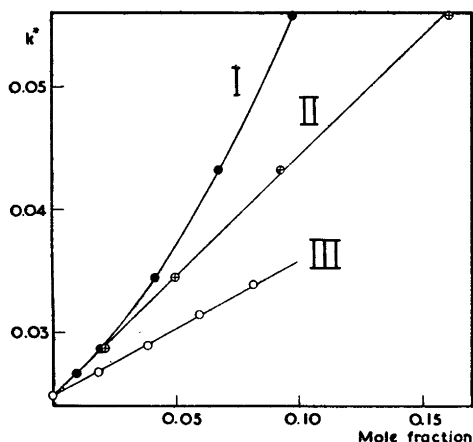
considerable contraction is found when dioxane and water are mixed (Hovorka, Schaefer, and Dreisbach [12]), and the viscosity-concentration curve for mixture, of dioxane and water shows a maximum (Geddes [13], Mariani [14]). While Geddes explains the maximum by the assumption of a pentahydrate of dioxanes Mariani concludes that a tetrahydrate is formed.

THE DISSOCIATION CONSTANT OF NITROACETIC ACID

The decomposition was studied in solutions of hydrochloric acid to which had been added either dioxane or glucose. The velocity constant is proportional to the degree of dissociation α of the nitroacetic acid. During the reaction, α increases a little and approaches a constant value α_∞ corresponding to an infinitely small concentration of nitroacetic acid. It has been shown earlier [4] how the velocity constant $\alpha_\infty k^*$ may be computed from the measurements.

The results are given in table 2. α_∞ has been computed by dividing $\alpha_\infty k^*$ with k^* found for an acetate buffer containing the non-electrolyte in the same concentration (table 1). The dissociation constant of nitroacetic acid is $K = a\alpha_\infty/(1-\alpha_\infty)$, where a is the concentration of hydrochloric acid. $-\log K$ found in this way is given in the next to the last column of table 2. $-\log K$ varies with the concentrations of both the non-electrolyte and the hydrochloric acid. In order to find $-\log K_a$, where K_a is the dissociation constant corresponding to pure aqueous solution of the non-electrolyte, extrapolations to zero ionic strength are carried out by means of formulae of the following form

$$-\log K = -\log K_a - A\mu^{\frac{1}{2}} + B\mu - C\mu^{\frac{3}{2}}, \qquad (1)$$

Table 2. The dissociation constant K of nitroacetic acid in aqueous solutions of dioxane and glucose at 18.0° C computed from the velocity constant $a_\infty k^*$ for the decomposition in solutions containing a molar hydrochloric acid.

Moles/l	a	$a_\infty k^*$	a_∞	μ	$-\log K$ found	$-\log K$ formula 1
Dioxane						
0.000	0.2003	0.003898	0.1571	0.2022	1.428	1.428
	0.09923	0.006428	0.2590	0.1024	1.460	1.460
	0.04049	0.01074	0.4327	0.0458	1.510	1.510
	0.04047	0.01074	0.4327	0.0458	1.510	1.510
	0.02009	0.01461	0.5886	0.0268	1.542	1.540
	0.02009	0.01465	0.5902	0.0270	1.539	1.540
0.999	0.2003	0.003370	0.1177	0.2017	1.573	1.573
	0.09923	0.005637	0.1968	0.1018	1.614	1.615
	0.09923	0.005646	0.1971	0.1017	1.613	1.615
	0.04047	0.00995	0.3474	0.0448	1.667	1.665
	0.02009	0.01432	0.5000	0.0259	1.697	1.698
1.998	0.2003	0.002866	0.08307	0.2014	1.741	1.741
	0.09923	0.004845	0.1404	0.1011	1.790	1.790
	0.04043	0.008867	0.2570	0.0436	1.854	1.853
	0.02009	0.01344	0.3896	0.0246	1.892	1.893
3.006	0.2003	0.002342	0.05413	0.2009	1.941	1.941
	0.09923	0.003954	0.09138	0.1004	2.001	2.002
	0.04051	0.007445	0.1721	0.0426	2.075	2.073
	0.02009	0.01185	0.2734	0.0226	2.122	2.123
4.003	0.2003	0.001837	0.03293	0.2007	2.166	2.167
	0.2003	0.001833	0.03286	0.2007	2.167	2.167
	0.09923	0.003112	0.05579	0.1000	2.232	2.234
	0.04049	0.005817	0.1043	0.0417	2.326	2.322
	0.02009	0.00953	0.1708	0.0218	2.383	2.385
Glucose						
1.000	0.2003	0.003028	0.1272	0.2018	1.535	1.535
	0.09931	0.005046	0.2120	0.1018	1.573	1.573
	0.04107	0.008780	0.3689	0.0453	1.620	1.620
	0.02009	0.01247	0.5239	0.0257	1.655	1.655
2.000	0.2003	0.002282	0.0985	0.2015	1.660	1.659
	0.09921	0.003875	0.1672	0.1012	1.701	1.704
	0.04107	0.006982	0.3013	0.0444	1.752	1.745
	0.02009	0.01046	0.4514	0.0249	1.782	1.786

where μ is the ionic strength. We assume that the Debye-Hückel limiting law holds for the solutions when μ is sufficiently small. It follows from this law that A may be calculated from the dielectric constant of the medium by means of the formula

$$A = 2 \times 1.824 \times 10^6 \, (\varepsilon T)^{-\frac{3}{2}},$$

where T is the absolute temperature. The dielectric constants for the dioxane solutions are found by interpolation from the data of Åkerlöf and Short [9], those for the glucose solutions from the determinations of Fürth as given by the International Critical Tables [11]. The other three constants of equation 1, namely B, C, and $-\log K_a$, are chosen so as to obtain the best agreement with $-\log K$ found from the measurements. The ionic strengths used for the computation are to be found in the fifth column of table 2. They are average values corresponding to solutions where one third of the nitroacetic acid originally added (about 0.02 molar) has been decomposed. ε and the constants of equation 1 are given in table 3. In the last column of table 2, the values of $-\log K$ calculated from equation 1 are presented.

Table 3. *The dissociation constant K of nitroacetic acid in aqueous solutions of dioxan and glucose at 18.0° C.*

$$-\log K = -\log K_a - A\mu^{\frac{1}{2}} + B\mu - C\mu^{\frac{3}{2}}.$$

Moles/l	Per cent	ε	A	B	C	$-\log K_a$
Dioxane						
0.000	0.00	81.13	1.006	1.103	0.218	1.677
0.999	8.73	73.28	1.170	1.767	1.143	1.845
1.998	17.34	65.45	1.388	2.031	1.223	2.065
3.006	25.91	57.62	1.680	2.772	2.035	2.320
4.003	34.29	49.93	2.082	3.396	2.307	2.625
Glucose						
1.000	16.90	59.6	1.596	3.218	2.61	1.839
2.000	31.82	40.5	2.850	7.806	7.81	2.072

$-\log K_a$ for nitroacetic acid in solutions of dioxane is given in the third column of table 4. A linear relation

$$-\log K_a = 1.677 + 0.1607 \, m, \tag{2}$$

where m is the molality of dioxane, is found to hold. $-\log K_a$ calculated from formula 2 is given in the fourth column of table 4.

Table 4. The dissociation constants of nitroacetic acid and acetic acid in aqueous solutions of dioxane at 18.0° C and zero ionic strength.

Molarity	Molality	$-\log K_a$ found	$-\log K_a$ form. 2	$-\log K_a$ form. 5	$-\log K_a$ acetic acid	Diff.
0.000	0.000	1.677	1.677	1.677	4.757	3.08
0.999	1.086	1.845	1.852	1.848	4.970	3.13
1.998	2.381	2.065	2.060	2.056	5.212	3.15
3.006	3.969	2.320	2.315	2.314	5.484	3.16
4.003	5.923	2.625	2.629	2.637	5.800	3.18

If the change in K_a for an uncharged acid when passing from one solvent to another were determined only by the change in electrostatic energy of the ions, and if the ions were unsolvated, rigid spheres (radii r_c and r_a) in a continuous medium, the following formula would hold (*cf.* Bjerrum and Larsson [15], Wynne-Jones [16], Brønsted [17])

$$-\log K_a = -\log K_{ao} + \frac{0.4343\ e^2}{kTr_m}\ (\varepsilon^{-1} - \varepsilon_0^{-1})$$

where e is the charge of the electron, k the Boltzmann's constant, r_m the average radius of the ions defined by

$$\frac{2}{r_m} = \frac{1}{r_c} + \frac{1}{r_a}$$

while K_{ao} is the dissociation constant and ε_0 the dielectric constant in a standard solvent, say water. If the values of e, k, and T are introduced we obtain

$$-\log K_a = -\log K_{ao} + \frac{249}{r_m}\ (\varepsilon^{-1} - \varepsilon_0^{-1}) \tag{3}$$

at 18° C., where r_m is expressed in Ångström's units.

If we take into account that the protons combine with water molecules forming hydroxonium ions, but assume that dioxane does not react with protons, we must replace K_a in formula 3 by $K_a \dfrac{a_{wo}}{a_w}$ or by $K_a \dfrac{p_o}{p}$, where a_w is the activity and p the partial vapour pressure of the water in the solution, a_{wo} the activity and p_o the vapour pressure of pure water. Adequate data for calculating this expression for the solutions examined here are, however, not available.

Instead of the activity we, therefore, use the molar concentration of water. We replace K_a in formula 3 by $K_a \dfrac{c_{wo}}{c_w}$. Since

$$\frac{c_{wo}}{c_w} = \frac{m}{c}$$

where m is the molality and c the molarity of the non-electrolyte added, we obtain

$$-\log \left(K_a \frac{m}{c}\right) = -\log K_{ao} + \frac{249}{r_m} (\varepsilon^{-1} - \varepsilon_0^{-1}) \qquad (4)$$

If this formula is valid, there is a linear dependence between $-\log \left(K_a \dfrac{m}{c}\right)$ and ε^{-1}. In order to test this on the data for nitroacetic acid in dioxane-water mixtures, $-\log \left(K_a \dfrac{m}{c}\right)$ has been plotted against ε^{-1}. The points fall close to a straight line of which the equation is

$$-\log \left(K_a \frac{m}{c}\right) = 1.677 + 102.6 (\varepsilon^{-1} - \varepsilon_0^{-1}) \qquad (5)$$

$-\log K_a$ calculated from formula 5 is presented in the fifth column of table 4. From the equations 4 and 5 we calculate $r_m = 249/102.6 = 2.4$ Å.

The dissociation constant of acetic acid in mixtures of dioxane and water has been determined electrometrically at different temperatures by Harned and Fallon [18]. The values given in the next to the last column of table 4 have been found by interpolation from their data. It is seen that the difference between $-\log K_a$ for acetic and nitroacetic acid, presented in the last column of table 4, is nearly constant and always greater than 3.

Table 5. The ratio f between the dissociation constant of nitroacetic acid in solutions of glucose calculated from formula 5 and that found from the measurements.

Molarity	Molality	$-\log K_a$ form. 5	$-\log K_a$ found	f
1.000	1.129	2.187	1.839	0.449
2.000	2.591	3.058	2.072	0.103

It is seen from table 5 that the dissociation constant of nitroacetic acid measured in solutions of glucose is much greater than that calculated from the

dielectric constant and the water concentration by means of the formula 5, holding for dioxane solutions. This difference is by no means surprising and may have different reasons. If, for instance, the protons combine not only with the water but also with the glucose molecules, an increase of K_a for glucose solutions will result. If this were the only reason for the difference, and if we further assume that no other cations than hydroxonium ions are formed to any appreciable extent in the dioxane solutions, the ratio f (given in the last column) between K_a calculated from formula 5 and K_a measured would be equal to the fraction of the protons which have formed hydroxonium ions $(f = c_{H_3O^+}/a)$.

SUMMARY

The kinetics of the decomposition of nitroacetic acid into nitromethane and carbon dioxide were studied (1) in acetate buffers containing dioxane, urea, glucose, or sucrose; and (2) in solutions of hydrochloric acid containing dioxane or glucose.

From the experiments in acetate buffers, the velocity constant k^* for the decomposition of the nitroacetate ion was computed. k^* increases when dioxane is added (124 per cent in 4 molar dioxane). Urea causes a smaller increase (37 per cent in 4 molar urea). When glucose is added, a moderate decrease of k^* is observed (7 per cent in 2 molar glucose), while sucrose has very little influence (2 per cent decrease in 2 molar sucrose). There is evidently no relation between k^* and the water concentration or the dielectric constant of the solution.

From the experiments on solutions of hydrochloric acid, the dissociation constant K_a for nitroacetic acid at zero ionic strength was computed. For the dioxane solutions, the formula $-\log K_a = 1.677 + 0.1607\, m$, where m is the molality, is found to hold, and there is a linear relation between $-\log \left(K_a \dfrac{c_{wo}}{c_w} \right)$ and the reciprocal of the dielectric constant. Here $\dfrac{c_{wo}}{c_w}$ is the ratio between the molar concentrations of water in pure water and in the solution. When solutions of the same dielectric constant are compared, $\left(K_a \dfrac{c_{wo}}{c_w} \right)$ is much greater in glucose than in dioxane solution. This may partly be due to the formation of glucosonium ions.

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