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The Effect of Metal Ions on the Rate of Decomposition of Nitroacetic Acid

KAI JULIUS PEDERSEN

Chemical Laboratory, Royal Veterinary and Agricultural College, Copenhagen, Denmark

It has been shown in earlier papers[1-4] that the rate-determining step in the decomposition of nitroacetic acid into nitromethane and carbon dioxide is an apparently spontaneous cleavage of the univalent ion

$$O_2N \cdot CH_2 \cdot COO^- \rightarrow {}^-OON : CH_2 + CO_2$$

The first dissociation constant of the acid is 0.0210 (at 18° C and zero ionic strength)[2,4], the second is about 10^{-9} (Heuberger[5]). The velocity constant for the decomposition of the univalent ion may therefore be found directly from measurements in acetate buffer solutions. A preliminary study of the effect of various salts added to the acetate buffers was made in the first paper[1]. It was found that the rate decreases considerably when certain cations (*e. g.* cupric ions) are added, while others (*e. g.* barium ions) have no, or only an insignificant effect. No satisfactory explanation of the effect could at that time be given, but it was suggested that the decrease in velocity is due to formation of complexes between the nitroacetate ion and the metal ions added. The nitroacetate ion decomposes spontaneously only when it is free. It is stable when it is bound either to a hydrogen ion or to a metal ion. The experiments in the present paper were carried out in order to test this explanation.

In the analysis of the effect of metal ions great difficulties are encountered. When the effect is studied in acetate buffer solutions it must be taken into account that most metal ions form complexes with acetate ions, and the extent of this complex formation is as a rule unknown. Only for cupric ions, fairly satisfactory data are available[6]. For this reason, only cupric ions were studied in acetate buffers. For the main part of the experiments were used unbuffered solutions of nitroacetic acid to which had been added a small amount of nitric acid (usually 0.002 molar). In these solutions, nitroacetic acid is only partly dissociated, and the degree of dissociation increases during reaction. In the following we shall deduce formulae by means of which a kinetic analysis may be carried out for such solutions.

EQUATIONS FOR CALCULATING VELOCITY CONSTANTS

We shall first examine the simple case when no complex-forming metal ion is present. Suppose that the solution contains h molar strong acid (*e. g.* nitric acid) and, at the time t minutes after the start, x molar nitroacetic acid of which the fraction α is present as univalent ion. α approaches α_∞ when x approaches zero (t infinity). When K denotes the dissociation constant of nitroacetic acid, we have

$$K = \frac{\alpha}{1-\alpha}\,(\mathrm{H}^+) = \frac{\alpha}{1-\alpha}\,(h + \alpha x) = \frac{\alpha_\infty}{1-\alpha_\infty}\,h$$

whence

$$\frac{1}{\alpha_\infty} = 1 + \frac{h}{K} \tag{1}$$

and

$$\frac{1}{\alpha} = \frac{1}{\alpha_\infty} + \frac{\alpha x}{K} \tag{2}$$

On multiplication by αx we obtain

$$x = \frac{1}{\alpha_\infty}\,(\alpha x) + \frac{1}{K}\,(\alpha x)^2 \tag{3}$$

from which we find

$$\alpha x = \frac{K}{2\alpha_\infty}\left[\sqrt{1 + \frac{4\,\alpha_\infty^{\,2}}{K}\,x} - 1\right] \tag{4}$$

Differentiation of equation 3 leads to

$$\mathrm{d}x = \frac{1}{\alpha_\infty}\,\mathrm{d}(\alpha x) + \frac{2}{K}\,(\alpha x)\,\mathrm{d}(\alpha x) \tag{5}$$

We assume that the velocity is proportional to αx:

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k\,(\alpha x)$$

On introducing equation 5 we obtain

$$- k \, \mathrm{d}t = \frac{1}{a_\infty} \, \mathrm{d}\ln(ax) + \frac{2}{K} \, \mathrm{d}(ax)$$

When we integrate this equation, introduce expression 4, and change to decadic logarithms, we find

$$^{*}a_\infty t + \text{const.} = 0.4343 \sqrt{1 + \frac{4 \, a_\infty^2}{K} \, x} + \log \left[\sqrt{1 + \frac{4 \, a_\infty^2}{K} \, x} - 1 \right] \tag{6}$$

where $k^* = 0.4343 \, k$.

The reaction is followed by measuring the pressure above the solution during the reaction. P, the difference between the final pressure reading and the reading at the time t, is proportional to x:

$$P = \varphi \, x \tag{7}$$

The proportionality factor φ may be found from the initial value of P and the known initial value of x: $\varphi = P_0/x_0$. If we use the abbreviation

$$\lambda = \frac{4 a_\infty^2}{K \varphi} \tag{8}$$

equation 6 may be written as follows

$$- k^* a_\infty t + \text{const.} = 0.4343 \sqrt{1 + \lambda P} + \log \left[\sqrt{1 + \lambda P} - 1 \right] \tag{9}$$

By means of this equation we may find k^* when K is known. a_∞ is given by equation 1.

If no strong acid has been added ($h = 0$, $a_\infty = 1$), equation 6 reduces to

$$- k^* t + \text{const.} = 0.4343 \sqrt{1 + \frac{4}{K} \, x} + \log \left[\sqrt{1 + \frac{4}{K} \, x} - 1 \right] \tag{10}$$

We shall now consider the case when complex-forming metal ions are present in the solution. We make the assumptions that one metal ion (Me^{++}) combines with only one univalent nitroacetate ion (HN^-):

$$Me^{++} + HN^{-} \rightleftharpoons MeHN^{+}$$

and that no other complexes of the ion Me^{++} are formed. When c denotes the stoicheiometric concentration of the metal ion added, α_1 the fraction of the total amount of nitroacetic acid which is bound to the metal ion, and K_1 the complexity constant, we have

$$K_1 = \frac{\alpha_1 x}{(c - \alpha_1 x)\, \alpha x}$$

from which we obtain

$$\alpha_1 = \frac{K_1 \alpha c}{1 + K_1 \alpha x} \qquad (11)$$

The dissociation constant of nitroacetic acid may be written as follows

$$K = \frac{\alpha}{1 - \alpha - \alpha_1} (h + \alpha x + \alpha_1 x),$$

from which we find

$$\frac{1 - \alpha - \alpha_1}{\alpha} = \frac{h}{K} + \frac{\alpha x}{K} + \frac{\alpha_1 x}{K} \qquad (12)$$

When equations 11 and 12 are introduced into the identity

$$\frac{1}{\alpha} = 1 + \frac{1 - \alpha - \alpha_1}{\alpha} + \frac{\alpha_1}{\alpha}$$

we obtain

$$\frac{1}{\alpha} = 1 + \frac{h}{K} + \frac{\alpha x}{K} + \frac{K_1 \alpha x c}{K\,(1 + K_1 \alpha x)} + \frac{K_1 c}{1 + K_1 \alpha x}$$

$$= 1 + \frac{h}{K} + \frac{\alpha x}{K} + \frac{c}{K} - \frac{(1 - KK_1)\, c}{K\,(1 + K_1\, \alpha x)}$$

$$= 1 + \frac{h}{K} + \frac{\alpha x}{K} + \frac{c}{K} - \frac{(1 - KK_1)(1 - K_1 \alpha x)\, c}{K\,(1 - K_1^2 \alpha^2 x^2)}$$

$K_1^2\alpha^2x^2$ in the denominator of the last term may be neglected since we shall apply the formula only to experiments where $x < 0.021$ and $K_1 < 3.2$. We therefore obtain

$$\frac{1}{a} = 1 + \frac{h}{K} + \frac{a\,x}{K} + \frac{c}{K} - \frac{(1 - KK_1)\,(1 - K_1\,a\,x)\,c}{K}$$

$$= 1 + \frac{h}{K} + K_1\,c + \frac{1}{K}\left[[1 + (1 - KK_1)\,K_1\,c\right]\,a\,x \qquad (13)$$

It follows from this equation that

$$\frac{1}{a_\infty} = 1 + \frac{h}{K} + K_1\,c \qquad (14)$$

Equation 13 may therefore be written as

$$\frac{1}{a} = \frac{1}{a_\infty} + \frac{1}{K}\left[1 + (1 - KK_1)\,K_1\,c\right]\,a\,x \qquad (15)$$

This equation is the same as equation 2 except that the constant factor before *ax* is different. On proceeding in the same way as in the simple case we therefore obtain an equation which may be written exactly as equation 9, but λ is here given by the expression

$$\lambda = \frac{4\,a_\infty^{\,2}}{K\,\varphi}\left[1 + (1 - KK_1)\,K_1\,c\right], \qquad (16)$$

and a_∞ by equation 14.

By means of equations 9, 14, and 16, we may directly find k^* when K and K_1 are known. Our problem is, however, to find K_1 when k^* and K are known. We therefore choose a reasonable value for K_1 and calculate the corresponding values of a_∞ and λ. We then compute k^*a_∞ from the measurements by means of equation 9, divide it by the known value of k^*, and introduce the obtained a_∞ into equation 14. If the value of K_1 found in this way does not agree with the chosen value, the computation is repeated on the basis of the new value, and so on until agreement is obtained.

In order to facilitate the computations by means of formula 9, values of the function

$$Y = 0.4343\,\sqrt{1 + X} + \log\,(\sqrt{1 + X} - 1) + 1$$

have been calculated for values of X from 2.00 to 0.01 with an interval of 0.01. They are given in Table 1.

Table 1. Values of the function

$$Y = 0.4343\sqrt{1+X} + \log\left(\sqrt{1+X} - 1\right) + 1$$

X	Y	Diff.	X	Y	Diff.	X	Y	Diff.	X	Y	Diff.
					35			45			64
2.00	1.6168	30	1.60	1.4874	36	1.20	1.3283	45	0.80	1.1162	64
1.99	1.6138	30	1.59	1.4838	36	1.19	1.3238	45	0.79	1.1098	64
1.98	1.6108	30	1.58	1.4802	36	1.18	1.3193	46	0.78	1.1034	66
1.97	1.6078	30	1.57	1.4766	36	1.17	1.3147	46	0.77	1.0968	66
1.96	1.6048	30	1.56	1.4730	36	1.16	1.3101	46	0.76	1.0902	66
1.95	1.6018	31	1.55	1.4694	36	1.15	1.3055	47	0.75	1.0836	68
1.94	1.5987	30	1.54	1.4658	37	1.14	1.3008	47	0.74	1.0768	69
1.93	1.5957	31	1.53	1.4621	37	1.13	1.2961	48	0.73	1.0699	69
1.92	1.5926	30	1.52	1.4584	37	1.12	1.2913	48	0.72	1.0630	70
1.91	1.5896	31	1.51	1.4547	37	1.11	1.2865	48	0.71	1.0560	71
1.90	1.5865	31	1.50	1.4510	38	1.10	1.2817	48	0.70	1.0489	72
1.89	1.5834	31	1.49	1.4472	38	1.09	1.2769	49	0.69	1.0417	73
1.88	1.5803	31	1.48	1.4434	38	1.08	1.2720	50	0.68	1.0344	74
1.87	1.5772	32	1.47	1.4396	38	1.07	1.2670	49	0.67	1.0270	74
1.86	1.5740	31	1.46	1.4358	38	1.06	1.2621	50	0.66	1.0196	76
1.85	1.5709	32	1.45	1.4320	38	1.05	1.2571	51	0.65	1.0120	77
1.84	1.5677	32	1.44	1.4282	39	1.04	1.2520	51	0.64	1.0043	78
1.83	1.5645	31	1.43	1.4243	39	1.03	1.2469	51	0.63	0.9965	79
1.82	1.5614	32	1.42	1.4204	39	1.02	1.2418	52	0.62	0.9886	80
1.81	1.5582	33	1.41	1.4165	40	1.01	1.2366	52	0.61	0.9806	82
1.80	1.5549	32	1.40	1.4125	39	1.00	1.2314	53	0.60	0.9724	82
1.79	1.5517	33	1.39	1.4086	40	0.99	1.2261	53	0.59	0.9642	84
1.78	1.5484	32	1.38	1.4046	40	0.98	1.2208	53	0.58	0.9558	85
1.77	1.5452	33	1.37	1.4006	41	0.97	1.2155	54	0.57	0.9473	87
1.76	1.5419	33	1.36	1.3965	40	0.96	1.2101	55	0.56	0.9386	88
1.75	1.5386	33	1.35	1.3925	41	0.95	1.2046	55	0.55	0.9298	89
1.74	1.5353	33	1.34	1.3884	42	0.94	1.1991	56	0.54	0.9209	91
1.73	1.5320	33	1.33	1.3842	41	0.93	1.1935	55	0.53	0.9118	92
1.72	1.5287	34	1.32	1.3801	41	0.92	1.1880	57	0.52	0.9026	94
1.71	1.5253	34	1.31	1.3760	42	0.91	1.1823	57	0.51	0.8932	96
1.70	1.5219	33	1.30	1.3718	43	0.90	1.1766	58	0.50	0.8836	98
1.69	1.5186	34	1.29	1.3675	42	0.89	1.1708	58	0.49	0.8738	99
1.68	1.5152	35	1.28	1.3633	43	0.88	1.1650	59	0.48	0.8639	101
1.67	1.5117	34	1.27	1.3590	43	0.87	1.1591	59	0.47	0.8538	104
1.66	1.5083	35	1.26	1.3547	43	0.86	1.1532	60	0.46	0.8434	105
1.65	1.5048	34	1.25	1.3504	44	0.85	1.1472	61	0.45	0.8329	107
1.64	1.5014	35	1.24	1.3460	43	0.84	1.1411	61	0.44	0.8222	110
1.63	1.4979	35	1.23	1.3417	45	0.83	1.1350	62	0.43	0.8112	112
1.62	1.4944	35	1.22	1.3372	44	0.82	1.1288	62	0.42	0.8000	115
1.61	1.4909	35	1.21	1.3328	45	0.81	1.1226	64	0.41	0.7885	117

Table 1 (continued).

X	Y	Diff.	X	Y	Diff.	X	Y	Diff.	X	Y	Diff.
0.40	0.7768	117	0.30	0.6419	152	0.20	0.4555	222	0.10	0.1440	425
0.39	0.7648	120	0.29	0.6261	158	0.19	0.4322	233	0.09	0.0972	468
0.38	0.7525	123	0.28	0.6098	163	0.18	0.4077	245	0.08	0.0450	522
0.37	0.7400	125	0.27	0.5930	168	0.17	0.3818	259	0.07	0.9859 − 1	591
0.36	0.7271	129	0.26	0.5756	174	0.16	0.3544	274	0.06	0.9178 − 1	681
0.35	0.7138	133	0.25	0.5575	181	0.15	0.3253	291	0.05	0.8377 − 1	801
0.34	0.7002	136	0.24	0.5388	187	0.14	0.2944	309	0.04	0.7396 − 1	981
0.33	0.6863	139	0.23	0.5193	195	0.13	0.2611	333	0.03	0.6136 − 1	1260
0.32	0.6719	144	0.22	0.4990	203	0.12	0.2253	358	0.02	0.4364 − 1	1772
0.31	0.6571	148	0.21	0.4777	213	0.11	0.1865	388	0.01	0.1346 − 1	3018
		152			222			425			

PROCEDURE AND MATERIALS

The experimental procedure was the same as in earlier papers [2–4]. The temperature was 18.0° C, and the initial concentration of nitroacetic acid was between 0.018 and 0.021 molar. The velocity constants given in the following tables are always average values from two separate runs with solutions of the same composition. The nitroacetic acid used for the measurements had the melting point 91.5—92° C. Standard solutions of the other substances were prepared from the purest commercial preparations, and the concentrations were in most cases checked by analysis. The standard solutions of beryllium, cadmium, and zinc nitrate were prepared by mixing equivalent amounts of solutions of the corresponding sulphates and barium nitrate.

THE VELOCITY CONSTANTS FOR THE DECOMPOSITION OF THE NITROACETATE ION AND THE DISSOCIATION CONSTANT OF NITROACETIC ACID

Table 2 shows the velocity constant k^* for the decomposition of the nitroacetate ion determined directly from measurements in acetate buffer solutions. It is seen that addition of up to 0.2 molar barium nitrate has no or only an insignificant influence on k^*.

Table 2. Decomposition of nitroacetic acid in 0.100 molar acetic acid, 0.100 molar sodium acetate, c molar barium nitrate.

c	k^*
0.000	0.02470
0.100	0.02449
0.200	0.02449

Table 3. Decomposition of nitroacetic acid in h molar nitric acid, 0.200 molar barium nitrate ($k^* = 0.02449$).

h	k^*a_∞	a_∞	K
0.09976	0.007716	0.3151	0.0459
0.04986	0.01174	0.4794	0.0460
0.01995	0.01708	0.6974	0.0460

Results of measurements in solutions containing 0.200 molar barium nitrate and various amounts of nitric acid are given in Table 3. In these solutions, the degree of dissociation α increases a little during reaction. The velocity constant $k^*\alpha_\infty$ corresponding to an infinitely small concentration of nitroacetic acid has been calculated by means of a formula given in an earlier paper [2]. When the value 0.02449 for k^* found above for acetate buffers is used, we find α_∞ and K given in the last two columns of Table 3. The measurements show that the dissociation constant of nitroacetic acid in 0.200 molar barium nitrate is 0.0460. It was found earlier [3] that it is 0.0210 at the ionic strength zero.

Table 4. Decomposition of nitroacetic acid in h molar nitric acid, 0.200 molar barium nitrate ($K = 0.0460$).

h	$1 + \frac{h}{K}$	α_∞	k^*a_∞	k^*
0.00100	1.0217	0.9788	0.02380	0.02432
0.00200	1.0435	0.9583	0.02339	0.02441
0.00992	1.2157	0.8226	0.02022	0.02458
0.01994	1.4335	0.6976	0.01721	0.02467

Table 4 gives a summary of results obtained for solutions containing 0.200 molar barium nitrate and from 0.001 to 0.02 molar nitric acid. The velocity constants $k^*\alpha_\infty$ and k^* were calculated by means of formula 9 with $K = 0.0460$. The agreement with k^* found directly from experiments in acetate buffers (Table 2) is fairly good.

One of the runs from Table 4 has been presented in more detail in Table 5 in order to illustrate the application and validity of formula 9. From the initial values $x_0 = 0.02039$ and $P_0 = 11.00$ (cm Hg), we find $\varphi = P_0/x_0 = 539.5$. The initial and final degrees of dissociation are, according to equations 1 and 4, $\alpha_0 = 0.731$ and $\alpha_\infty = 0.9583$. From equation 8 we obtain $\lambda = 0.1480$. $X = \lambda P$ is computed for all the values of P given in the table, and the corresponding values of Y are taken from Table 1. When Y is plotted against t we obtain the linear equation given at the top of the table. Hence, it follows

Table 5. Decomposition of nitroacetic acid in 0.00200 molar nitric acid, 0.200 molar barium nitrate.

$x_0 = 0.02039$, $P_0 = 11.00$, $\varphi = 539.5$, $K = 0.0460$.
$a_0 = 0.731$, $a_\infty = 0.9583$, $\lambda = 0.1480$.
$Y = 1.4663 - 0.02335\, t$. $k^* a_\infty = 0.02335$, $k^* = 0.02436$.

t	P(obs.)	Y	P(calc.)	$\Delta \cdot 10^2$
1	10.54	1.4730	10.59	+ 5
2	10.15	1.4518	10.16	+ 1
3	9.75	1.4293	9.74	− 1
4	9.35	1.4061	9.34	− 1
5	8.94	1.3814	8.95	+ 1
6	8.56	1.3577	8.58	+ 2
7	8.23	1.3363	8.22	− 1
8	7.86	1.3116	7.87	+ 1
9	7.55	1.2900	7.53	− 2
10	7.18	1.2634	7.21	+ 3
11	6.88	1.2409	6.89	+ 1
12	6.58	1.2175	6.59	+ 1
13	6.31	1.1957	6.30	− 1
14	6.04	1.1731	6.03	− 1
15	5.75	1.1478	5.76	+ 1
16	5.49	1.1242	5.50	+ 1
17	5.25	1.1014	5.25	0
18	5.01	1.0778	5.02	+ 1
19	4.77	1.0529	4.79	+ 2
20	4.57	1.0317	4.57	0
21	4.35	1.0072	4.36	+ 1
23	3.95	0.9597	3.97	+ 2
25	3.58	0.9116	3.60	+ 2
27	3.27	0.8679	3.27	0
29	2.97	0.8218	2.97	0
31	2.69	0.7745	2.69	0
33	2.45	0.7305	2.44	− 1
35	2.23	0.6863	2.21	− 2
37	2.03	0.6425	2.00	− 3
39	1.84	0.5969	1.81	− 3
44	1.45	0.4875	1.40	− 5

that $k^* a_\infty = 0.02335$, and $k^* = 0.02436$. When we start from the linear equation just mentioned, and carry out the computations in the opposite order, we find the values of P given in the fourth column of the table. The differences between the calculated and observed values of P are given in the last column. The agreement is satisfactory.

THE EFFECT OF METAL IONS IN SOLUTIONS CONTAINING NITRIC ACID

The decomposition was studied in solutions of the salts: cupric, beryllium, cadmium, lead, nickel, zinc, cobaltous, magnesium, calcium, and aluminium nitrate. The solutions contained 0.001 or 0.002 molar nitric acid, except in the case of aluminium and beryllium nitrate where the concentration of nitric acid was raised to 0.01 and 0.02 in order to repress hydrolysis. The solutions contained further sufficient barium nitrate for maintaining nearly the same ionic strength (0.6) in all the solutions (calculated on the assumption of complete dissociation). A summary of the composition of the solutions and the results obtained is given in Table 6.

In the computations we have for the velocity constant of the nitroacetate ion k^* used the value found previously (Table 4) for 0.200 molar barium nitrate and the same concentration of nitric acid as in the solution considered. For the dissociation constant of nitroacetic acid K we have always taken the value 0.0460 found for 0.200 molar barium nitrate (Table 3).

Two of the runs, one with cupric and one with aluminium nitrate, are presented in more detail in Tables 7 and 8. The tables show only the last step in the computation based on the method of successive approximations. From the supposed value of K_1 given at the top of the tables, we find $^1/\alpha_\infty$ and λ by means of equations 14 and 16. From the observed values of P we compute $X = \lambda\ P$ and find in Table 1 the corresponding values of Y. When Y for each of the experiments is plotted against t, the points fall close to a straight line of the equation given at the top of the table. Since Y expresses the right side of equation 9, the numerical value of the coefficient to t gives us $k^*\alpha_\infty$. When the known value of k^* is introduced we find $^1/\alpha_\infty$. Finally, we compute K_1 by means of equation 14. In the column headed P (calc.) are given values of P calculated on the basis of the linear equations at the top of the tables. The listed values of $\Delta = P(\text{calc.}) — P(\text{obs.})$ show that the measurements agree well with equation 9.

The results for all the solutions examined are summarized in Table 6. The values found for K_1 are given in the next to the last column, while mean values of K_1 for each of the 10 ions examined are presented at the top of the table. $k^*\alpha_\infty$ calculated from the mean values of K_1 is given in the last column of the table.

It is seen from Table 6 that the concentrations of nitric acid used for repressing the hydrolysis of the beryllium and aluminium ion are sufficient. If they were not, the values of K_1 would decrease with increasing h. The tendency goes rather in the opposite direction. The hydrolysis of the other ions examined is, even at the small concentrations of nitric acid used here, so weak that it is of no importance.

Table 6. Decomposition of nitroacetic acid in c molar solutions of the salts mentioned below. The solutions contained in addition d molar barium nitrate and h molar nitric acid.

Mean values of complexity constants K_1 computed from the measurements:

Cu^{++}	Be^{++}	Cd^{++}	Pb^{++}	Ni^{++}	Zn^{++}	Co^{++}	Mg^{++}	Ca^{++}	Al^{+++}
2.77	1.82	1.54	1.39	1.14	1.08	1.00	0.65	0.50	3.05

	c	d	h	k^*a_∞	$^1/a_\infty$	K_1	k^*a_∞(calc.)
$Cu(NO_3)_2$	0.1999	0.000	0.00200	0.01519	1.607	2.82	0.01528
	0.1596	0.040	0.00200	0.01632	1.496	2.83	0.01643
	0.1195	0.080	0.00200	0.01796	1.359	2.61	0.01776
	0.0798	0.120	0.00200	0.01926	1.267	2.81	0.01930
	0.0798	0.120	0.00100	0.01956	1.243	2.78	0.01955
	0.0399	0.160	0.00200	0.02118	1.152	2.73	0.02115
$Be(NO_3)_2$	0.200	0.000	0.00992	0.01555	1.581	1.82	0.01556
	0.150	0.050	0.01995	0.01442	1.711	1.85	0.01445
	0.150	0.050	0.00992	0.01654	1.486	1.80	0.01651
	0.100	0.100	0.01995	0.01518	1.625	1.92	0.01527
	0.100	0.100	0.00992	0.01770	1.389	1.73	0.01759
$Cd(NO_3)_2$	0.200	0.000	0.00200	0.01792	1.362	1.59	0.01806
	0.150	0.050	0.00200	0.01912	1.277	1.55	0.01915
	0.100	0.100	0.00200	0.02042	1.195	1.52	0.02038
	0.050	0.150	0.00200	0.02202	1.108	1.30	0.02178
$Pb(NO_3)_2$	0.200	0.000	0.00200	0.01852	1.318	1.37	0.01847
	0.150	0.050	0.00200	0.01945	1.255	1.41	0.01950
	0.100	0.100	0.00200	0.02062	1.184	1.40	0.02064
	0.050	0.150	0.00200	0.02192	1.114	1.40	0.02193
$Ni(NO_3)_2$	0.1983	0.000	0.00200	0.01914	1.275	1.17	0.01923
	0.1492	0.050	0.00200	0.02013	1.213	1.13	0.02011
	0.0992	0.100	0.00200	0.02111	1.156	1.14	0.02110
	0.0498	0.150	0.00200	0.02228	1.096	1.05	0.02218
$Zn(NO_3)_2$	0.1981	0.000	0.00200	0.01938	1.260	1.09	0.01941
	0.1486	0.050	0.00200	0.02036	1.199	1.05	0.02027
	0.0990	0.100	0.00200	0.02136	1.143	1.00	0.02122
	0.0496	0.150	0.00200	0.02206	1.107	1.27	0.02225
$Co(NO_3)_2$	0.200	0.000	0.00200	0.01954	1.249	1.03	0.01963
	0.200	0.000	0.00100	0.01992	1.221	1.00	0.01991
	0.150	0.050	0.00200	0.02035	1.200	1.04	0.02045
	0.100	0.100	0.00200	0.02132	1.145	1.01	0.02135
	0.050	0.150	0.00200	0.02250	1.085	0.83	0.02232

Table 6 (continued)

	c	d	h	k^*a_∞	$^1/a_\infty$	K_1	k^*a_∞(calc.)
$Mg(NO_3)_2$	0.200	0.000	0.00200	0.02073	1.178	0.67	0.02080
	0.100	0.100	0.00200	0.02208	1.106	0.62	0.02202
$Ca(NO_3)_2$	0.200	0.000	0.00200	0.02135	1.143	0.50	0.02131
	0.100	0.100	0.00200	0.02229	1.095	0.52	0.02230
$Al(NO_3)_3$	0.1006	0.000	0.01995	0.01408	1.752	3.16	0.01417
	0.1006	0.000	0.00992	0.01614	1.523	3.05	0.01614
	0.0503	0.100	0.01995	0.01557	1.584	3.00	0.01554
	0.0503	0.100	0.00992	0.01805	1.362	2.90	0.01795

Table 7. Decomposition of nitroacetic acid in 0.00200 molar nitric acid, 0.1999 molar cupric nitrate.

$x_0 = 0.02008$, $P_0 = 10.74$, $\varphi = 534.9$, $k^* = 0.02441$, $K = 0.0460$.
Suppose that $K_1 = 2.803$, hence $^1/a_\infty = 1.6038$, $\lambda = 0.09405$.
$Y = 1.2410 - 0.01522\ t$, $k^*a_\infty = 0.01522$, $^1/a_\infty = 1.6038$, $K_1 = 2.803$.

t	P(obs.)	P(calc.)	$\Delta\ 10^2$	t	P(obs.)	P(calc.)	$\Delta\ 10^2$
1	10.52	10.52	0	18	6.32	6.31	− 1
2	10.22	10.22	0	20	5.93	5.93	0
3	9.93	9.92	− 1	22	5.59	5.57	− 2
4	9.62	9.63	+ 1	24	5.23	5.23	0
5	9.36	9.35	− 1	26	4.91	4.91	0
6	9.08	9.08	0	28	4.62	4.61	− 1
7	8.83	8.82	− 1	30	4.32	4.32	0
8	8.56	8.56	0	32	4.04	4.05	+ 1
9	8.31	8.30	− 1	34	3.81	3.80	− 1
10	8.04	8.06	+ 2	36	3.53	3.56	+ 3
11	7.82	7.82	0	38	3.31	3.34	+ 3
12	7.60	7.59	− 1	40	3.14	3.12	− 2
13	7.36	7.36	0	42	2.92	2.93	+ 1
14	7.12	7.14	+ 2	44	2.74	2.74	0
15	6.90	6.92	+ 2	46	2.59	2.56	− 3
16	6.71	6.71	0	48	2.41	2.40	− 1
17	6.50	6.51	+ 1	50	2.24	2.24	0

In the computation of K_1 we have assumed that K, the dissociation constant of nitroacetic acid, is 0.0460 for all the solutions, the same as for a solution of barium nitrate of the same ionic strength. This assumption is to some extent justified by the good agreement with formula 9 obtained in all the experiments. The rate depends on both K and K_1, but the influence of the former decreases gradually during the reaction owing to the disappearance

Table 8. Decomposition of nitroacetic acid in 0.01995 molar nitric acid, 0.1006 molar aluminium nitrate.

$x_0 = 0.01913,\ P_0 = 10.18,\ \varphi = 532.1,\ k^* = 0.02467,\ K = 0.0460.$
Suppose that $K_1 = 3.07$, hence $^1/a_\infty = 1.7425,\ \lambda = 0.0681.$
$Y = 1.0448-0.01416\ t,\ k^*a_\infty = 0.01416,\ ^1/a_\infty = 1.7422,\ K_1 = 3.07.$

t	P(obs.)	P(calc.)	$\Delta\ 10^2$	t	P(obs.)	P(calc.)	$\Delta\ 10^2$
1	9.82	9.91	+ 9	20	5.70	5.69	− 1
2	9.61	9.63	+ 2	22	5.37	5.36	− 1
3	9.38	9.36	− 2	24	5.04	5.04	0
4	9.10	9.10	0	26	4.76	4.75	− 1
5	8.84	8.84	0	28	4.49	4.47	− 2
6	8.60	8.59	− 1	30	4.21	4.20	− 1
7	8.33	8.34	+ 1	32	3.93	3.95	+ 2
8	8.11	8.10	− 1	34	3.72	3.72	0
9	7.89	7.87	− 2	36	3.50	3.50	0
10	7.63	7.65	+ 2	39	3.18	3.19	+ 1
11	7.41	7.42	+ 1	42	2.90	2.90	0
12	7.21	7.21	0	45	2.63	2.64	+ 1
14	6.80	6.80	0	48	2.42	2.41	− 1
16	6.42	6.41	− 1	51	2.20	2.19	− 1
18	6.02	6.04	+ 2	54	2.00	1.99	− 1

of hydrogen ions. The plot of Y against t would therefore fall on a curved line if a wrong value of K were chosen. In none of the experiments a systematic deviation from linearity was observed. The agreement with formula 9 was, as a rule, of a similar quality as that shown in Tables 7 and 8.

We shall examine the influence of the value chosen for K a little closer, and choose for that purpose the experiment presented in Table 7. It follows from the table that the measurements are in agreement with formula 9 when $K = 0.0460$ and $K_1 = 2.80$. The true values of α are therefore those calculated from equation 13 when these values for K and K_1 are introduced. They are given in Table 9 for three values of x, corresponding to the beginning, the middle, and the end of the run. If we choose another value of K we may calculate the corresponding value of K_1 from the values of α by means of equation 13. Finally, we may calculate k^*a_∞ by means of equation 14 and the known value of k^*. The results of the computation for different values of K are given in Table 9. It is seen that the "velocity constant" k^*a_∞ varies with x when a wrong value of K is chosen.

Summarizing, we may say that the results obtained for solutions containing nitric acid and various metal salts agree with the assumption that only the free univalent nitroacetate ion decomposes while its complexes with either

Table 9. K_1 *and* k^*a_∞ *calculated from different values of* K *for the experiment presented in Table 7.*

x	a	Assumed values of K: 0.0300	0.0400	0.0460	0.0500	0.0600
		Calculated values of K_1:				
0.0200	0.5161	2.01	2.56	2.80	2.94	3.22
0.0100	0.5602	2.27	2.65	2.80	2.89	3.02
0.0000	0.6235	2.69	2.77	2.80	2.82	2.85
		Calculated values of k^*a_∞:				
0.0200		0.01662	0.01563	0.01522	0.01499	0.01455
0.0100		0.01605	0.01544	0.01522	0.01509	0.01491
0.0000		0.01522	0.01522	0.01522	0.01522	0.01522

hydrogen or metal ions are stable. In order to explain the measurements quantitatively it is sufficient to assume that complexes of one metal ion and one nitroacetate ion are formed, and that the complexity constants K_1 have the values given at the top of Table 6 (at the ionic strength 0.6). To the list may be added the complexity constant for the hydrogen ion $K_1 = 1/0.0460 \doteq 21.7$, and that for the barium ion $K_1 = 0$.

THE EFFECT OF CUPRIC IONS IN ACETATE BUFFER SOLUTIONS

The effects of a series of metal salts on the decomposition of nitroacetic acid in acetate buffer solutions were studied already in the paper from 1927[1]. The quantitative results obtained are however of little interest because the extent of complex formation between the metal ions and the acetate ion is unknown, and because the effect of changes in the concentrations of the buffer constituents were not examined. Data which make it possible to estimate the extent of complex formation for cupric ions are now available[6]. New experiments on the effect of cupric ions were therefore carried out, and an attempt was made to give a quantitative interpretation of the results.

When nitroacetic acid is dissolved in an acetate buffer solution, an equivalent amount of acetate ion is transformed into acetic acid. For this reason, both the hydrogen and the cupric ion concentration decreases during reaction. We shall see that the rate depends not only on the concentration of free cupric ion, but (contrary to expectation) also on the hydrogen and acetate ion concentrations. Since all three concentrations change, the first-order law will not hold exactly. For most of the solutions examined (see Table 10a),

Table 10 a. The effect of cupric ions on the decomposition of nitroacetic acid in acetate buffer solutions. The table gives the stoicheiometric concentrations before the addition of nitroacetic acid and the first-order velocity constant k^*a.

No.	CH_3COOH	CH_3COONa	$Cu(NO_3)_2$	$Ba(NO_3)_2$	$NaNO_3$	k^*a
1	0.798	0.2983	0.09985	0.000	0.000	0.02133
2	0.3988	0.2983	0.09985	0.000	0.000	0.02030
3	0.1994	0.2983	0.09985	0.000	0.000	0.01816
4	0.0994	0.2983	0.09985	0.000	0.000	0.01556
5	0.798	0.1993	0.04990	0.050	0.100	0.02288
6	0.4990	0.1993	0.04990	0.050	0.100	0.02237
7	0.3988	0.1993	0.04990	0.050	0.100	0.02227
8	0.1994	0.1993	0.04990	0.050	0.100	0.02102
9	0.0994	0.1993	0.04990	0.050	0.100	0.01912
10	0.798	0.1993	0.09985	0.000	0.100	0.02081
11	0.3988	0.1993	0.09985	0.000	0.100	0.01990
12	0.1994	0.1993	0.09985	0.000	0.100	0.01817
13	0.0994	0.1993	0.09985	0,000	0.100	0.01598
14	0.3988	0.0996	0.04990	0.050	0.200	0.02153
15	0.1994	0.0996	0.04990	0.050	0.200	0.02139
16	0.0994	0.0996	0.04990	0.050	0.200	0.01971
17	0.1994	0.0996	0.09985	0.000	0.200	0.01843
18	0.1994	0.1993	0.07480	0.025	0.100	0.01960
19	0.1994	0.1993	0.02486	0.075	0.100	0.02284
20	0.1994	0.1993	0.00000	0.100	0.100	0.02488

the concentrations of the buffer components were so large that no systematic deviation from a straight line could be detected when log P was plotted against t, but in some cases a small but distinct curvature was seen. An average slope was found, and it was assumed that its numerical value is equal to the velocity constant k^*a corresponding to $x = 0.01$, that is, to the solution when about one half of the nitroacetic acid is decomposed. The velocity constants k^*a found in this way are given in the last column of Table 10a. The velocity constant for experiment no. 20 is equal to k^* since no cupric salt is present in the solution ($a = 1$). a for the rest of the experiments may therefore be found by dividing their velocity constants by that for experiment no. 20.

In order to compute the concentrations of free cupric and acetate ion when $x = 0.01$, we use the complexity constants K_1', K_2', and K_3' for the complexes $CuAc^+$, $CuAc_2$, and $CuAc_3^-$, respectively (where Ac^- denotes acetate ion).

Table 10 b. The effect of cupric ions on the decomposition of nitroacetic acid in acetate buffer solutions. Concentrations corresponding to $x = 0.01$ (about half decomposition). The velocity constant k^*a calculated by means of equation 21 and $k^* = 0.02488$.

No.	μ	(Cu^{++})	(Ac^-)	$\frac{(Ac^-)}{(HAc)}$	$\frac{1-a}{a\,(Cu^{++})}$	k^*a (calc.)	Percentage diff.
1	0.369	0.00802	0.1474	0.1824	20.7	0.02147	+ 0.7
2	0.369	0.00796	0.1478	0.3615	28.3	0.02027	− 0.1
3	0.369	0.00782	0.1487	0.7101	47.3	0.01833	+ 0.9
4	0.369	0.00765	0.1498	1.369	78.3	0.01556	0
5	0.491	0.00555	0.1244	0.1540	15.7	0.02280	− 0.4
6	0.491	0.00550	0.1247	0.2450	20.4	0.02238	0
7	0.491	0.00550	0.1247	0.3050	21.3	0.02209	− 0.8
8	0.491	0.00542	0.1252	0.5979	33.9	0.02085	− 0.8
9	0.491	0.00528	0.1261	1.1527	57.1	0.01889	− 1.2
10	0.408	0.01790	0.0802	0.0993	10.9	0.02091	+ 0.5
11	0.408	0.01776	0.0805	0.1969	14.1	0.01996	+ 0.3
12	0.408	0.01751	0.0810	0.3868	21.1	0.01838	+ 1.1
13	0.408	0.01721	0.0816	0.7459	32.4	0.01601	+ 0.2
14	0.522	0.01535	0.0487	0.1191	10.1	0.02195	+ 1.9
15	0.522	0.01533	0.0487	0.2326	10.6	0.02112	− 1.3
16	0.522	0.01501	0.0491	0.4488	17.5	0.01977	+ 0.3
17	0.480	0.04430	0.0289	0.1378	7.9	0.01869	+ 1.4
18	0.446	0.01043	0.1007	0.4809	25.8	0.01948	− 0.6
19	0.543	0.00208	0.1549	0.7397	43	0.02260	− 1.1

The following formulae have been found[6] to hold when the ionic strength μ is less than 0.4:

$$
\begin{aligned}
\log K_1' &= 2.164 - 1.992\sqrt{\mu}/(1 + 1.8\sqrt{\mu}) \\
\log K_2' &= 3.17 \ - 2.988\sqrt{\mu}/(1 + 2\sqrt{\mu}) \\
K_3' &= K_2'
\end{aligned}
\tag{17}
$$

We shall use these formulae although the ionic strength for most of the solutions exceeds 0.4. The stoicheiometric concentration of cupric ion c is first corrected for the amount bound to nitroacetate ion. If it is assumed that each stabilized nitroacetate ion binds one cupric ion we find that the concentration of cupric ion which is either free or bound to acetate ions is $c' = c - 0.01(1-a)$ when $x = 0.01$. The ionic strengths of the solutions and their concentrations of free cupric and acetate ion, computed by means of equations 17, are given in the second, third, and fourth column of Table 10b. In the next column is presented the ratio $(Ac^-)/(HAc)$, where (HAc) has been calculated by adding 0.01 to the concentration of acetic acid before nitroacetic acid was dissolved.

We shall first examine whether the total effect may be explained alone by the formation of the complex $CuHN^+$ according to the scheme

$$Cu^{++} + HN^- \rightleftharpoons CuHN^+ \tag{18}$$

where HN^- denotes nitroacetate ion. In this case we have

$$\frac{1-\alpha}{\alpha\,(Cu^{++})} = \frac{x-(HN^-)}{(HN^-)\,(Cu^{++})} = \frac{(CuHN^+)}{(HN^-)\,(Cu^{++})} = K_1$$

In the previous section of the paper it was found that $K_1 = 2.77$ when $\mu = 0.6$. Here μ varies from 0.37 to 0.54. We should therefore expect to find $(1-\alpha)/\alpha(Cu^{++})$ equal to about 3 for all the solutions, but actually it varies from 7.9 to 78 (see the sixth column of Table 10b). Formation of the complex $CuHN^+$ is therefore far from sufficient to explain the whole effect.

The first 16 experiments in Table 10b fall in four groups with nearly constant μ, (Cu^{++}), and (Ac^-). Average values are given in Table 11. If we plot $(1-\alpha)/\alpha(Cu^{++})$ against $(Ac^-)/(HAc)$, the points fall, for each of the four groups, close to a straight line of the equation

$$\frac{1-\alpha}{\alpha\,(Cu^{++})} = A + B\,\frac{(Ac^-)}{(HAc)} \tag{19}$$

where A and B have the values given in Table 11. Since the ratio $(Ac^-)/(HAc)$ is inversely proportional to the hydrogen ion concentration, this indicates the existence of the equilibrium

$$CuHN^+ \rightleftharpoons CuN + H^+ \tag{20}$$

Formation of the two complexes $CuHN^+$ and CuN is, however, not sufficient for explaining the total effect. If this were the case, the points for all the four groups would fall close to the *same* straight line, and A would have a value of about 3. An examination shows that both A and B increase approximately linearly with the acetate ion concentration (see Table 11). As a result of the analysis we obtain the equation

Table 11. A and B of equation 19.

A(calc.) = 3.0 + 54 (Ac$^-$). B(calc.) = 14.3 + 232 (Ac$^-$).

Nos.	μ	(Cu^{++})	(Ac$^-$)	A	B	A (calc.)	B (calc.)
1– 4	0.369	0.00786	0.1484	11.0	49.9	11.0	48.7
5– 9	0.491	0.00545	0.1250	9.4	41.4	9.8	43.3
10–13	0.408	0.01760	0.0808	7.5	34.5	7.4	33.0
14–16	0.522	0.01523	0.0488	5.6	26.5	5.7	25.6

$$\frac{1-\alpha}{\alpha\,(\mathrm{Cu}^{++})} = 3.0 + 54\ (\mathrm{Ac}^-) + \left[14.3 + 232\ (\mathrm{Ac}^-)\right] \frac{(\mathrm{Ac}^-)}{(\mathrm{HAc})} \qquad (21)$$

which holds with good approximation for all the experiments. This is seen from Table 10b where $k^*\alpha$ calculated by means of formula 21 is presented in the next to the last column, while the last column shows the percentage difference between the calculated value and that found directly from the measurements.

In order to explain formula 21 we must assume that also the following two equilibria contribute to the stabilisation of the nitroacetate ion:

$$\mathrm{Cu}^{++} + \mathrm{HN}^- + \mathrm{Ac}^- \rightleftharpoons \mathrm{CuHNAc} \qquad (22)$$

$$\mathrm{CuHNAc} \rightleftharpoons \mathrm{CuNAc}^- + \mathrm{H}^+ \qquad (23)$$

When K_{HAc} denotes the dissociation constant of acetic acid, and the mass action constants for the equilibria 18, 20, 22, and 23 are designated as K_1, K_2, K_3, and K_4, respectively, we obtain

$$(\mathrm{CuHN}^+) = K_1\ (\mathrm{Cu}^{++})\ (\mathrm{HN}^-) \qquad (24)$$

$$(\mathrm{CuN}) = K_2 \frac{(\mathrm{CuHN}^+)}{(\mathrm{H}^+)} = \frac{K_1 K_2}{K_{\mathrm{HAc}}}\ (\mathrm{Cu}^{++})\ (\mathrm{HN}^-) \frac{(\mathrm{Ac}^-)}{(\mathrm{HAc})} \qquad (25)$$

$$(\mathrm{CuHNAc}) = K_3\ (\mathrm{Cu}^{++})\ (\mathrm{HN}^-)\ (\mathrm{Ac}^-) \qquad (26)$$

$$(\mathrm{CuNAc}^-) = K_4 \frac{(\mathrm{CuHNAc})}{(\mathrm{H}^+)} = \frac{K_3 K_4}{K_{\mathrm{HAc}}}\ (\mathrm{Cu}^{++})\ (\mathrm{HN}^-) \frac{(\mathrm{Ac}^-)^2}{(\mathrm{HAc})} \qquad (27)$$

$$\frac{1-\alpha}{\alpha\,(\mathrm{Cu}^{++})} = \frac{x - (\mathrm{HN}^-)}{(\mathrm{HN}^-)\ (\mathrm{Cu}^{++})} = \frac{(\mathrm{CuHN}^+) + (\mathrm{CuHNAc}) + (\mathrm{CuN}) + (\mathrm{CuNAc}^-)}{(\mathrm{HN}^-)\ (\mathrm{Cu}^{++})}$$

$$= K_1 + K_3\,(\mathrm{Ac}^-) + \left[\frac{K_1K_2}{K_{\mathrm{HAc}}} + \frac{K_3K_4}{K_{\mathrm{HAc}}}\,(\mathrm{Ac}^-)\right]\frac{(\mathrm{Ac}^-)}{(\mathrm{HAc})} \qquad (28)$$

Comparison with formula 21 shows that

$$K_1 = 3.0 \qquad K_3 = 54 \qquad \frac{K_1K_2}{K_{\mathrm{HAc}}} = 14.3 \qquad \frac{K_3K_4}{K_{\mathrm{HAc}}} = 232 \qquad (29)$$

If we as an estimate of K_{HAc} at the ionic strengths concerned[6] use the value 3.5×10^{-5}, we obtain

$$K_2 = 1.7 \times 10^{-4} \text{ and } K_4 = 1.5 \times 10^{-4}$$

K_2 and K_4 are the strength constants of the acids $CuHN^+$ and CuHNAc, respectively. As we should expect, both constants are much larger than the acid strength of the free nitroacetate ion, $K_{HN^-} = 10^{-9}$. It is, however, a little surprising that the difference between K_2 and K_4 is not greater.

K_1 was in experiments on solutions containing nitric acid found to have the value 2.77 at the ionic strength 0.6. Since we may expect that K_1 decreases a little with increasing μ, the value $K_1 = 3.0$ found here is reasonable. We may compare K_1 with the complexity constant K_1' of the acetato complex $CuAc^+$ which, at the same ionic strength, according to the first of the equations 17, is about 36. We see that the acetate ion is bound faster than the less basic nitroacetate ion although the ratio $K_1'/K_1 = 12$ is much smaller than the ratio of their base strengths (about 1.3×10^3).

The two balanced reactions

$$CuHN^+ + Ac^- \rightleftharpoons CuHNAc$$

and

$$CuAc^+ + Ac^- \rightleftharpoons CuAc_2$$

have the equilibrium constants $K_3/K_1 = 18$ and $K_2'/K_1' = 6$, respectively. If the tendency to bind an acetate ion were the same whether a nitroacetate ion or an acetate ion were already present in the complex, the former constant would be twice as great as the latter (owing to the statistical effect of the two acetate ions present in $CuAc_2$). Actually, it is three times as great. The nitroacetato complex has therefore a somewhat greater tendency to bind an acetate ion than has the acetato complex. This consideration shows that the value found for K_3 is not unreasonable.

The cupric ion binds the divalent nitroacetate ion with great strength. This is seen from the following rough estimate of the complexity constant for the complex CuN:

$$\frac{(\mathrm{CuN})}{(\mathrm{Cu}^{++})\,(\mathrm{N}^{--})} = \frac{K_1 K_2}{K_{\mathrm{HN}^-}} = \frac{3.0 \times 1.7 \times 10^{-4}}{10^{-9}} = 5 \times 10^{5}$$

It follows from equations 24—29 that we may expect that all the numerical coefficients in equation 21 decrease with increasing ionic strength. For that reason, the effect should decrease (k^*a increase) with increasing μ, provided that (Cu^{++}), (Ac^-), and (H^+) are the same. In the solutions examined, μ varies from 0.37 to 0.54. The accuracy of the measurements is, however, not great enough to show the influence of the ionic strength.

We have seen that the measurements in solutions containing nitric acid could be explained satisfactorily without taking into account the dissociation $\mathrm{CuHN}^+ \rightleftharpoons \mathrm{CuN} + \mathrm{H}^+$. Let us consider the experiment in which c has its highest value (0.2), and which therefore is most sensitive to the effect of the acid dissociation. From the data in Table 7 we find that (H^+) during the measurements decreases from 0.018 to 0.0058. If we apply equation 21 to an acetate-free solution we must replace (Ac^-)/(HAc) by $K_{\mathrm{HAc}}/(\mathrm{H}^+)$. When we set $K_{\mathrm{HAc}} = 3.5 \times 10^{-5}$, we obtain

$$\frac{1 - a}{a\,(\mathrm{Cu}^{++})} = 3.0 + \frac{5 \times 10^{-4}}{(\mathrm{H}^+)} = 3.0\left(1 + \frac{1.7 \times 10^{-4}}{(\mathrm{H}^+)}\right)$$

When we neglect the dissociation of the ion CuHN^+ we shall therefore in the experiment shown in Table 7 find a value of K_1 which is between 1 and 3 per cent too high, but this corresponds to less than 1 per cent in a.

SUMMARY

The rate-determining reaction in the decomposition of nitroacetic acid is a spontaneous cleavage of the free univalent nitroacetate ion. The ion is stable when it is bound either to a hydrogen or a metal ion.

Formulae for the kinetic analysis of the reaction in unbuffered solutions containing no or only a small concentration of strong acid, have been deduced. In order to facilitate the use of the formulae values of the function

$$Y = 0.4343\,\sqrt{1 + X} + \log\left(\sqrt{1 + X} - 1\right) + 1$$

have been calculated for values of X from 2.00 to 0.01 (Table 1).

The kinetic effects of the metal ions mentioned below were studied in solutions of their nitrates. The solutions contained sufficient barium nitrate to maintain an ionic strength of 0.6, and, further, 0.002 or 0.001 (in the cases of Al^{+++} and Be^{++}, 0.02 or 0.01) molar nitric acid. The decrease in velocity may be explained by assuming that complexes of one metal ion and one nitroacetate ion with the following complexity constants (K_1) are formed:

H^+	Al^{+++}	Cu^{++}	Be^{++}	Cd^{++}	Pb^{++}	Ni^{++}	Zn^{++}	Co^{++}	Mg^{++}	Ca^{++}	Ba^{++}
21.7	3.05	2.77	1.82	1.54	1.39	1.14	1.08	1.00	0.65	0.50	0

The effect of cupric ions has also been studied in acetate buffer solutions. The influence of the formation of complexes between cupric and acetate ions has been taken into account, and it has been shown that the kinetic effect may be explained by the following equilibria (HN^- and Ac^- denote nitroacetate and acetate ion, respectively):

$$Cu^{++} + HN^- \overset{K_1}{\rightleftharpoons} CuHN^+ \overset{K_2}{\rightleftharpoons} CuN + H^+$$

$$Cu^{++} + HN^- + Ac^- \overset{K_3}{\rightleftharpoons} CuHNAc \overset{K_4}{\rightleftharpoons} CuNAc^- + H^+$$

with the equilibrium constants (ionic strength about 0.45):

$$K_1 = 3.0, \quad K_2 = 1.7 \times 10^{-4}, \quad K_3 = 54, \quad \text{and } K_4 = 1.5 \times 10^{-4}$$

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