

## Stability Constants of Metal Ion — Hydroxylamine Complexes in Aqueous Solution

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The first formation constants of the metal ions Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) with hydroxylamine have been determined from pH-measurements at very small concentrations of hydroxylamine ( $\bar{n} \leq 0.02$ ) and compared with available data from the literature on the influence of the decomposition of hydroxylamine of the same metal ions.

Some ligands such as hydroxylamine, hydrazine and the reductones, which are known to form complexes with metal ions, also undergo decomposition.<sup>1-3</sup> This decomposition always results in oxidation of the ligand; in the case of copper(II) and ascorbic acid it is known,<sup>3</sup> that the metal ion is reduced but is reoxidized by oxygen dissolved in the solution. The extent to which complexes participate in these decomposition reactions is unknown and the work reported here is an attempt to investigate this.

The stabilities of the 1:1 complexes of hydroxylamine with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Ag(I) have been measured and are compared with differences in the influence of several of these metal ions on the rate of oxidation of hydroxylamine in aqueous solutions in the presence of oxygen, as reported by Audrieth and Moews.<sup>1</sup>

### EXPERIMENTAL

The stabilities of metal ion-hydroxylamine 1:1 complexes were determined by pH-titration in an aqueous solution of sodium nitrate. Each solution contained initially 0.004991 M hydroxylamine *p*-toluene sulphonic acid salt, 0.0500 M nitrate solution of the complex forming metal and the ionic strength was kept at a constant value of  $\mu = 0.5$  M by addition of the calculated amount of sodium nitrate. The reference electrode was an 0.5 M potassium chloride calomel electrode, and contact was made with the titrating

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solution by means of an 0.5 M sodium nitrate salt bridge. The titrations were carried out with 0.5 M carbonate free sodium hydroxide solution. Before each titration the glass electrode was checked by titrating a known amount of a strong acid under similar conditions, as has been described in detail by Schwarzenbach.<sup>4</sup> The  $-\log[\text{H}^+]$  values were measured with a Radiometer pH-meter, type 4, using a Radiometer glass electrode, type G.202.C, comparing with a standard acid titration, in the same salt medium. For addition of alkali an "Ingold Ultramicroburette", type Normal 2 with total capacity of 1 ml was used, and by this means 0.001 ml of solution could be transferred with an accuracy of  $\pm 0.05\%$ . The temperature of the system was kept at  $20.0 \pm 0.1^\circ\text{C}$ , using a "Lauda Ultrathermostate".

The titrations were carried out by mixing the hydroxylamine *p*-toluene sulphonic acid salt and the sodium nitrate solution, required to maintain the ionic strength constant, in the thermostated vessel (of 25 ml volume). To these solutions was added the aliquot amount of 0.5 M sodium hydroxide from the Ingold microburette. After the system had equilibrated in the presence of the glass electrode and the 0.5 M sodium nitrate bridge, 5.00 ml of the 0.25 M nitrate solution of the complex forming metal was added and the  $-\log[\text{H}^+]$  value measured. Every titration point was prepared and measured separately. In the case of copper(II) it was necessary to measure the change of the  $-\log[\text{H}^+]$  values with time and to extrapolate to zero time (Table 1).

With all other metal ions the reduction was too slow to affect the results, *i.e.* the  $-\log[\text{H}^+]$  values remained constant at least 3 min.

In the present work the following symbols are used:

- $c_{\text{hx}}$ : the total concentration of hydroxylamine *p*-toluene sulphonic acid salt.  
 $c_{\text{M}}$ : the total concentration of the metal ion.  
 $[\text{H}^+]$ : the concentration of the free hydrogen ion.  
 $[\text{hx}]$ : the concentration of the hydroxylamine base.  
 $[\text{Hhx}^+]$ : the concentration of the protonated hydroxylamine.  
 $[\text{M}(\text{hx})_i]$ : the concentration of the complex  $\text{M}(\text{hx})_i$ .  
 $c_{\text{NaOH}}$ : the total concentration of sodium hydroxide.

All concentrations are calculated in mole/liter (= M).

$\rho = [\text{Hhx}^+]/c_{\text{hx}}$ : the protonation degree of hydroxylamine.

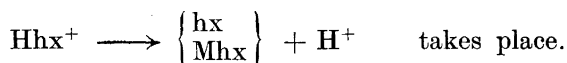
$$\bar{n} = \frac{\sum_i [\text{M}(\text{hx})_i]}{c_{\text{M}}} \quad \text{the formation function, defined by Bjerrum.}^5$$

The equilibrium constants are defined by the expressions:

$$K_{\text{Hhx}} = \frac{[\text{Hhx}^+]}{[\text{H}^+] \cdot [\text{hx}]} : \text{the formation constant of Hhx}^+.$$

$$K_{\text{M}(\text{hx})_i} = \frac{[\text{M}(\text{hx})_i]}{[\text{M}(\text{hx})_{i-1}] \cdot [\text{hx}]} : \text{the } i\text{'th formation constant of } \text{M}(\text{hx})_i.$$

*Calculation.* The so called "excess curves" have been evaluated, as described by Schwarzenbach.<sup>4</sup> One can assume, that during the neutralization process, in the presence of the metal ion, under the present conditions, the reaction



For this reaction the virtual equilibrium constant  $K'$  can be defined as

$$K' = \frac{([\text{hx}] + [\text{Mhx}]) \cdot [\text{H}^+]}{[\text{Hhx}^+]}$$

The protonation degree of the ligand can here be written as:

$$p = \frac{c_{\text{hx}} - [\text{H}^+] - c_{\text{NaOH}}}{c_{\text{hx}}}$$

As the concentration of the deprotonated acid is identical with the sum of the concentrations of the free base and the bound ligand, the virtual constant  $K'$  becomes:

$$K' = \frac{1-p}{p} \cdot [\text{H}^+]$$

and the stability of the complex  $\text{Mhx}$  can be calculated using the equation

$$K_{\text{Mhx}} = \frac{K' \cdot K_{\text{Hhx}} - 1}{c_{\text{M}}}$$

The calculation of the formation function  $\bar{n}$  by the method of Bjerrum<sup>5</sup> gives another method of calculating the formation constants:

$$[\text{Hhx}^+] = c_{\text{hx}} - [\text{H}^+] - c_{\text{NaOH}}$$

$$[\text{hx}] = \frac{[\text{Hhx}^+]}{K_{\text{Hhx}} \cdot [\text{H}^+]}$$

$$[\text{Mhx}] = c_{\text{hx}} - [\text{Hhx}^+] - [\text{hx}]$$

$$\bar{n} = \frac{[\text{Mhx}]}{c_{\text{M}}} \quad \text{and, as } c_{\text{M}} \gg c_{\text{hx}}, \quad K_{\text{Mhx}} = \frac{\bar{n}}{[\text{hx}]}$$

The results used to calculate the stability constants for copper(II) were those in Table 1 after extrapolation to zero time. The exact course of the redox reaction observed was not investigated. The amount of complex formation is always very small ( $\bar{n} \leq 0.02$ ).

*Analysis.* The hydroxylamine *p*-toluene sulphonic acid salt was analysed by the following methods:

The hydroxylamine was determined by the method of Bray *et al.*<sup>6</sup>

The total concentration of the anion was determined indirectly as chloride.

The *p*-toluene sulphonic acid salt was converted to the chloride form by means of an anion exchange resin (Amberlite IRA-400, analytical grade) and titrated potentiometrically with silver nitrate solution. The method was checked using hydroxylamine hydrochloride and *p*-toluene sulphonic acid.

The silver ion analyses were carried out by potentiometric titration with sodium chloride solution.

The other cations were determined by complexometric titration (Schwarzenbach<sup>7</sup>). The use of murexide as indicator to determine the endpoint in the case of copper analyses has the advantage that copper(II) can be determined in the presence of copper(I). This method can be used to demonstrate that the reduction of copper(II) by hydroxylamine is, under the conditions of the experiments, slow and hence one can extrapolate to zero time and find the true value for the stability constant of the complex  $\text{Cu hx}^{2+}$ .

*Equipment.* The equipment, used here is described in detail elsewhere, *e.g.* Szilárd.<sup>8</sup>

Table 1. Variation of  $-\log[\text{H}^+]$  with time in a system, which contains 0.004991 M hydroxylamine *p*-toluene sulphonic acid salt, 0.0500 copper(II) nitrate,  $\mu = 0.5$  M ( $\text{NaNO}_3$ ),  $t = 20.0 \pm 0.1^\circ\text{C}$ .

$c_{\text{NaOH}}$	Time in minutes:					
	0	1	2	3	4	5
0.000000	3.63	3.60	3.57	3.54	3.52	3.50
0.000101	3.72	3.68	3.64	3.61	3.57	3.54
0.000202	3.83	3.77	3.71	3.66	3.62	3.59
0.000303	3.94	3.85	3.77	3.71	3.66	3.63
0.000404	4.02	3.93	3.85	3.79	3.75	3.71
0.000505	4.10	4.00	3.90	3.84	3.79	3.76
0.000605	4.17	4.04	3.95	3.89	3.85	3.82
0.000706	4.25	4.12	4.00	3.95	3.91	3.89
0.000807	4.30	4.18	4.09	4.04	4.00	3.98
0.000908	4.34	4.22	4.13	4.09	4.06	4.04

## DATA AND RESULTS

The Table 2 contains the experimental results for the determination of the formation constant of the hydroxylammonium ion. These results were found by titration of an 0.004991 M hydroxylamine *p*-toluene sulphonic salt solution with 0.5 M sodium hydroxide under the same conditions as in the determination of the stability constants.

Table 3 contains the measured  $-\log[\text{H}^+]$  values for the different complexes. The use of the Ingold Ultramicroburette made it possible to choose the same sodium hydroxide concentrations for all the titration series.

Attempts to determine by means of the so called "equivalent-curves"<sup>4</sup> the formation constants of the higher complexes of copper(II) and silver(I) were not satisfactory, since the  $-\log[\text{H}^+]$  differences were relatively small and the rates of the redox reactions too high. It was only possible to estimate the following values:

$$\log K_{\text{Cu}(\text{hx})_2^+} \sim 1.7 \quad \text{and} \quad \log K_{\text{Ag}(\text{hx})_2^+} < 3.$$

On the basis of the deviations in the  $\log K_{\text{Mhx}}$  values of any simple formation constant, their error is about  $\pm 0.1 \log K$  unit.

Table 2.  $c_{\text{hx}} = 0.004991$  M,  $\mu = 0.5$  M ( $\text{NaNO}_3$ ),  $t = 20.0 \pm 0.1^\circ\text{C}$ .

$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	$p$	$\log K_{\text{Hhx}}$
0.000000	4.22	0.988	6.12
0.000101	4.55	0.974	6.12
0.000202	4.78	0.956	6.12
0.000303	4.95	0.938	6.12
0.000404	5.07	0.917	6.11
0.000505	5.18	0.897	6.12
0.000605	5.27	0.878	6.12
0.000706	5.34	0.858	6.12
0.000807	5.42	0.837	6.13
0.000908	5.47	0.817	6.12

Table 3.  $c_{\text{hx}} = 0.004991 \text{ M}$ ,  $c_{\text{M}} = 0.0500 \text{ M}$ ,  $\mu = 0.5 \text{ M}$  ( $\text{NaNO}_3$ ),  $t = 20.0 \pm 0.1^\circ\text{C}$ .  
 $\text{M} = \text{Mn(II)}$

$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
0.000000	4.18	0.0000563	0.9987	0.00019	3.18	0.50
0.000101	4.49	0.0001130	0.9733	0.00041	3.60	0.56
0.000202	4.72	0.0001892	0.9557	0.00064	3.34	0.52
0.000303	4.89	0.0002731	0.9367	0.00086	3.14	0.50
0.000404	5.00	0.0003449	0.9170	0.00138	4.00	0.60
0.000505	5.11	0.0004347	0.8972	0.00156	3.58	0.55
0.000605	5.20	0.0005226	0.8772	0.00179	3.42	0.53
0.000706	5.28	0.0006138	0.8573	0.00194	3.18	0.50
0.000807	5.34	0.0006883	0.8371	0.00247	3.58	0.55
0.000908	5.41	0.0007891	0.8170	0.00246	3.12	0.50

$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
M = Co(II)						
0.000000	4.14	0.0000512	0.9985	0.00042	7.84	0.89
0.000101	4.42	0.0000964	0.9721	0.00085	8.86	0.95
0.000202	4.64	0.0001569	0.9549	0.00136	8.64	0.94
0.000303	4.82	0.0002332	0.9362	0.00170	7.28	0.86
0.000404	4.91	0.0002802	0.9165	0.00272	9.72	0.99
0.000505	5.03	0.0003611	0.8969	0.00306	8.48	0.93
0.000605	5.12	0.0004350	0.8770	0.00356	8.20	0.91
0.000706	5.20	0.0005105	0.8571	0.00404	7.90	0.90
0.000807	5.25	0.0005596	0.8369	0.00506	9.04	0.96
0.000908	5.31	0.0006263	0.8168	0.00573	9.16	0.96

$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
M = Ni(II)						
0.000000	4.03	0.0000395	0.9813	0.00108	27.2	1.43
0.000101	4.25	0.0000649	0.9685	0.00185	28.5	1.45
0.000202	4.43	0.0000963	0.9521	0.00286	29.6	1.47
0.000303	4.56	0.0001273	0.9337	0.00406	32.0	1.51
0.000404	4.69	0.0001687	0.9149	0.00511	30.3	1.48
0.000505	4.78	0.0002028	0.8954	0.00638	31.4	1.50
0.000605	4.88	0.0002495	0.8759	0.00738	29.5	1.47
0.000706	4.94	0.0002798	0.8560	0.00875	31.3	1.50
0.000807	5.04	0.0003446	0.8362	0.00943	27.4	1.44
0.000908	5.09	0.0003776	0.8161	0.01077	28.5	1.45

$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
M = Cu(II)						
0.000000	3.63	0.0000153	0.9531	0.00437	285	2.45
0.000101	3.72	0.0000186	0.9415	0.00547	295	2.47
0.000202	3.83	0.0000236	0.9299	0.00652	276	2.44
0.000303	3.94	0.0000299	0.9169	0.00769	257	2.41
0.000404	4.02	0.0000354	0.8998	0.00928	262	2.42
0.000505	4.10	0.0000417	0.8828	0.01085	260	2.41
0.000605	4.17	0.0000481	0.8650	0.01250	260	2.41
0.000706	4.25	0.0000567	0.8471	0.01411	249	2.38
0.000807	4.30	0.0000623	0.8292	0.01577	253	2.40
0.000908	4.34	0.0000665	0.8085	0.01775	267	2.43

M = Zn(II)						
$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
0.000000	4.18	0.0000563	0.9987	0.00019	3.18	0.50
0.000101	4.50	0.0001159	0.9734	0.00033	2.86	0.46
0.000202	4.73	0.0001933	0.9558	0.00055	2.84	0.46
0.000303	4.89	0.0002731	0.9367	0.00086	3.14	0.50
0.000404	5.02	0.0003612	0.9171	0.00105	2.88	0.46
0.000505	5.11	0.0004347	0.8972	0.00156	3.58	0.55
0.000605	5.21	0.0005354	0.8773	0.00153	2.84	0.46
0.000706	5.27	0.0006000	0.8573	0.00223	3.70	0.57
0.000807	5.35	0.0007054	0.8372	0.00212	3.00	0.48
0.000908	5.41	0.0007891	0.8170	0.00346	3.12	0.50

M = Ag(I)						
$c_{\text{NaOH}}$	$-\log[\text{H}^+]$	[hx]	$p$	$\bar{n}$	$K_{\text{Mhx}}$	$\log K_{\text{Mhx}}$
0.000000	3.90	0.0000291	0.9745	0.00194	67.2	1.83
0.000101	4.06	0.0000416	0.9623	0.00293	70.3	1.85
0.000202	4.20	0.0000565	0.9469	0.00417	73.9	1.87
0.000303	4.35	0.0000786	0.9303	0.00538	68.3	1.83
0.000404	4.46	0.0000989	0.9120	0.00680	68.8	1.84
0.000505	4.54	0.0001166	0.8929	0.00834	71.5	1.85
0.000605	4.58	0.0001248	0.8733	0.01014	81.2	1.91
0.000706	4.61	0.0001309	0.8534	0.01199	91.5	1.96
0.000807	4.65	0.0001398	0.8335	0.01379	99.8	2.00

## DISCUSSION

Nyman<sup>9</sup> measured the stabilities of the zinc-hydroxylamine complexes. His value for the first constant ( $\log K_{\text{Mhx}} = 0.4$ ) agrees within the experimental error with that from the present measurements. The existence of the copper(II)-hydroxylamine and silver(I)-hydroxylamine associations seems to indicate, that during the oxidation of a ligand by a metal ion, such temporary associations probably always are formed to a certain extent. It may also be possible to show the existence of similar associations in aqueous solutions with hydrazine and the reductones.

In Table 4 the percent decomposed hydroxylamine ( $c_{\text{hx}} = 0.4$  M) in the presence of 0.0001 M metal sulphate, in oxygen atmosphere, after 21 h, as reported by Audrieth and Moews<sup>1</sup> (first column), is compared with the  $K_{\text{Mhx}}$  values, determined in the present work at  $\mu = 0.5$  ( $\text{NaNO}_3$ ) and  $t = 20.0 \pm 0.1^\circ\text{C}$  (second column). Due to the different experimental conditions a quantitative comparison is not possible, but it can be seen from Table 4, that there seems to be some relationship between the figures in the two columns.

Yoneda<sup>10</sup> has studied complexes of hydroxylamine (hx) and measured what he supposed to be the spectra of  $[\text{Co}(\text{hx})_6]^{3+}$  and  $[\text{Ni}(\text{hx})_6]^{2+}$  in concentrated hydroxylamine-hydroxylammonium solution, 6 M and 2 M, respectively. He pointed out, that these complexes could be intermediates in the oxidation reaction of the ligands. As pointed out by Audrieth and Moews,<sup>1</sup> the role of dissolved oxygen may be important for such reactions. On this topic there are

Table 4.

Metal ion:	% decomposed hydroxylamine after Audrieth and Moews <sup>1</sup> :	$K_{Mhx}$ 0.5 (NaNO <sub>3</sub> ), $t = 20^\circ\text{C}$ .
Mn(II)	41	3.2
Co(II)	57	8.0
Ni(II)		32
Fe(II)	53	
Cu(II)	100 (?)	250
Zn(II)	37	3.2
Ag(I)		80

a great number of unsolved problems, such as the "catalytic influence" of the hydroxyl ion on the decomposition of the hydroxylamine. If the associations, which are pointed out in the present paper, are decisive for the oxidation reactions of such ligands, one has to take into consideration, that their concentration increases with higher hydroxyl ion concentration. This could give an adequate explanation of the "catalytic influence" of the hydroxyl ion concentration in such redox reactions.

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