

Thermodynamics of the Ionization of Hydroxylamine and Nitrous Acid in Water

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The ionization constants of hydroxylamine and nitrous acid in aqueous sodium perchlorate solutions have been determined potentiometrically at 15°, 20°, 25°, and 35°C. The thermodynamic ionization constants of the protolytes at these temperatures were obtained by extrapolating the data to zero ionic strength. The values of the free energies, enthalpies, entropies, and heat capacities of the protolytic equilibria were evaluated from the values of the thermodynamic ionization constants. The results are discussed.

In a recent paper¹ we discussed previously determined values of the ionization constant of nitrous acid in aqueous solutions. We have since extended our measurements to determine the effect of temperature on the protolysis of nitrous acid and the results are presented here.

Several studies have been made also on the protolysis of hydroxylamine in water,² but the results of the various workers are rather inconsistent and we therefore considered it worth while to study the protolyses of this amine once more.

EXPERIMENTAL

Nitrous acid. The methods, apparatus and reagents used in the determination of the ionization constant of nitrous acid were the same as in the previous study¹ of the ionization of nitrous acid at 25°C. The cells were of the following type (molarities at 20°C):



In the table below are given the compositions of different solutions of ionic strength 0.25 at 20°C used in the previous paper:¹

Ionic strength <i>I</i>	Ref. el. M NaCl	Titrant 0.1 M CH ₃ COOH 0.03 M NaNO ₃ M NaClO ₄	Ref. buff. 0.005 M HClO ₄ 0.03 M NaNO ₃ M NaClO ₄	Stud. sol. 0.01 M NaNO ₂ 0.03 M NaNO ₃ M NaClO ₄
0.25	0.25	0.22	0.215	0.21

The present measurements at 15°, 20°, and 35°C were performed on solutions of the same compositions.

Hydroxylamine. Hydroxylamine hydrochloride (guaranteed reagent, E. Merck A.G.) was used as such. Sodium perchlorate (G. F. Smith Co.) was purified as described in the previous paper¹ and the dried product was kept in a desiccator. The ionic strengths of the solutions were adjusted with sodium perchlorate. The cells used in the potentiometric titrations were of the type (20°C):



The solutions were titrated in a nitrogen atmosphere with about 0.1 M (carbonate-free) NaOH solutions ($I-0.1$) M in NaClO₄, which were checked against potassium biphthalate (guaranteed reagent, E. Merck A. G.) potentiometrically. The measurements were performed at 15°, 20°, 25°, and 35° ± 0.01°C and at four ionic strengths. The glass electrode was a Beckman No. 41260. The other reagents were also of analytical reagent grade (E. Merck A. G.).

Because of the possible decomposition of hydroxylamine in solution,³ the solutions were titrated as soon as possible (within about an half hour) after dissolving of hydroxylamine.

The solutions used in the titrations had the following compositions (at 20°C):

Ionic strength <i>I</i>	Ref. elect. 0.01 M NaCl M NaClO ₄	Titrant ~0.1 M NaOH M NaClO ₄	Ref. buff. sol. 0.005 M HClO ₄ M NaClO ₄	Studied solution 0.01 M NH ₂ OH.HCl M NaClO ₄
0.04	0.03	—	0.035	0.03
0.25	0.24	0.15	0.245	0.24
1.00	0.99	0.90	0.995	0.99
2.25	2.240	2.15	2.245	2.24

The pH values of the buffer solutions were taken to be 2.301 at 15°, 20°, and 25° and 2.303 at 35°C. An error of ± 0.5 mV in the potential measurements causes an error of about ± 0.009 unit in the p*K* value of hydroxylamine.

The results at the ionic strength of about 0.04 were obviously erroneous (the values of p*K* were too low) because of the diffusion potentials and are not reported. For further details, see Ref. 1.

RESULTS AND DISCUSSION

A. The ionization of nitrous acid. The needed ionization constants of acetic acid were calculated from the equation⁴

$$pK = pK_0 - 2A\sqrt{I}/(1 + 1.597\sqrt{I}) + 0.2446 I \quad (1)$$

where the constants *A* and p*K*₀ have the following values:

<i>t</i> ° C	<i>A</i>	p <i>K</i> ₀ ⁵
15	0.5028	4.7587
20	0.5070	4.7570
35	0.5211	4.7650

The thermodynamic values (p*K*₀) of the ionization constant of nitrous acid were obtained by extrapolating the determined p*K* values to zero ionic strength using the equation:¹

$$pK = pK_0 - 2A\sqrt{I}/(1 + 1.622\sqrt{I}) + 0.261 I \quad (2)$$

The values of the constant A were the same as above. The experimental data are presented in Table 1 and the results of the calculations in Table 2. The

Table 1. Potentiometric determination of the protolysis constant of nitrous acid in aqueous sodium perchlorate solutions at 15°, 20°, and 35°C. The data given are $\text{pH} = -\log[\text{H}^+]$ and ml (20°C) of titrant added ($I = 0.25$). The pH values are mean values from four measurements.

Titrant ml	pH		
	15°C	20°C	35°C
4.0	4.046	4.026	3.986
4.5	4.013	4.001	3.949
5.0	3.995	3.974	3.927
5.5	3.965	3.947	3.900
6.0	3.941	3.923	3.878
6.5	3.919	3.898	3.856
7.0	3.899	3.887	3.840
7.5	3.880	3.864	3.822
8.0	3.863	3.845	3.804
8.5	3.846	3.827	3.788
9.0	3.829	3.813	3.773
9.5	3.815	3.800	3.758
10.0	3.802	3.789	3.743

Table 2. The determined values of pK and the extrapolated values of pK_0 of nitrous acid at different temperatures.

$t^\circ \text{C}$	I	pK	pK_0
15	0.2504	3.018	3.230
20	0.2501	2.989	3.203
25	0.2498	2.951	3.148
35	0.2491	2.890	3.113

Table 3. Values of the ionization constant of nitrous acid determined at different temperatures by various authors.

$^\circ\text{C}$	Ionic strength (added salt)	$-\log K$	Method	Ref.
0	low	3.49	conductivity	6
12.5	»	3.34	»	6
15	0	3.23	gl. elect.	This work
20	0	3.20	»	»
25	0	3.15	»	»
25	variable	3.35	conductivity	7
25	»	3.4	kinetic	8
25	»	3.19	analytical	9
25	low	3.29	conductivity	10
25	1 (NaClO_4)	2.80	spectrophotometric	11
30	low	3.22	conductivity	6
35	0	3.11	gl. elect.	This work
50	low	3.15	conductivity	10

values of pK at 15°, 20°, and 35°C are mean values of fifty-two experimental data from four titration curves. The previous values¹ determined at 25°C are also included in Table 2.

Table 3 shows values of the ionization constant of nitrous acid determined at different temperatures by various authors. Closest to the present values are those of Bauer⁹ and Schmid *et al.*¹⁰ at 25°C. Our value¹ of pK at 25°C and $I = 1$ (NaClO_4) is 3.02 as compared with the value 2.80 determined by Vassian and Eberhardt¹¹ under the same conditions.

B. The ionization of hydroxylamine. The protolysis of hydroxylamine in the acid range may be presented as



Table 4. Potentiometric titrations of hydroxylamine solutions of ionic strength $I \sim 0.25$ (20°C). 100 ml of solution 0.01 M in $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 0.24 M in NaClO_4 titrated with a 0.09933 M NaOH solution 0.15 M in NaClO_4 . The number of millilitres of NaOH solution added is given above and the pH below.

Titration No.	Temp.											
1	15°C	ml	3.002	3.505	4.017	4.502	5.000	5.502	6.001	6.500	7.005	
		pH	5.840	5.941	6.039	6.123	6.212	6.294	6.380	6.474	6.579	
2		ml	3.004	3.500	3.999	4.501	5.001	5.500	6.002	6.506	7.003	
		pH	5.799	5.908	6.007	6.100	6.193	6.282	6.378	6.478	6.578	
3		ml	3.002	3.500	4.002	4.500	5.002	5.502	6.007	6.501	7.020	
		pH	5.831	5.929	6.034	6.119	6.210	6.296	6.387	6.483	6.595	
4	20°C		3.002	3.521	4.001	4.540	5.050	5.501	6.008	6.502	7.024	
			5.714	5.822	5.908	6.004	6.097	6.176	6.267	6.364	6.468	
5			3.000	3.509	4.001	4.500	5.001	5.512	6.001	6.509	7.000	
			5.715	5.817	5.910	5.996	6.082	6.176	6.262	6.360	6.462	
6			3.003	3.502	4.001	4.500	5.009	5.500	6.001	6.500	7.021	
			5.714	5.815	5.908	5.997	6.087	6.175	6.260	6.360	6.469	
7	25°C		3.018	3.520	4.025	4.611	5.001	5.502	6.025	6.521		
			5.611	5.709	5.808	5.908	5.979	6.072	6.165	6.260		
8			3.026	3.502	4.002	4.500	5.002	5.502	6.002	6.511	7.000	
			5.607	5.702	5.793	5.883	5.971	6.062	6.152	6.251	6.346	
9			3.004	3.505	4.020	4.520	5.002	5.500	6.012	6.510	7.020	
			5.597	5.695	5.792	5.878	5.964	6.054	6.147	6.241	6.338	
10	35°C		3.001	3.518	4.000	4.501	5.022	5.501	5.999	6.518	7.108	
			5.398	5.502	5.595	5.682	5.776	5.855	5.942	6.042	6.163	
11			3.006	3.504	4.002	4.500	5.039	5.500	6.001	6.500	6.999	
			5.383	5.484	5.578	5.666	5.761	5.841	5.928	6.019	6.124	
12			3.061	3.504	4.000	4.504	5.000	5.500	6.002	6.501	7.009	
			5.393	5.474	5.566	5.664	5.746	5.816	5.891	6.003	6.107	

for which the mass action law gives the ionization constant

$$K = [\text{H}^+][\text{NH}_2\text{OH}]/[\text{NH}_3\text{OH}^+] \quad (4)$$

and

$$\text{p}K = \text{p}H - \log\{(C_B + [\text{H}^+])/[C - (C_B - [\text{H}^+])]\} \quad (5)$$

where $\text{p}H = -\log[\text{H}^+]$, C_B is the total concentration of the added strong base and C is the total concentration of hydroxylamine.

Table 5. Potentiometric titrations of hydroxylamine solutions of ionic strength $I \sim 1.00$ (20°C). 100 ml of solution 0.01 M in $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 0.99 M in NaClO_4 titrated with a 0.09911 M NaOH solution 0.90 M in NaClO_4 . The number of millilitres of NaOH solution added is given above and the pH below.

Titration No.												
13	15°C	ml	3.007	3.505	4.001	4.512	5.009	5.500	6.039	6.501	7.021	
		pH	5.892	6.000	6.097	6.195	6.278	6.369	6.469	6.560	6.669	
14		ml	3.022	3.504	4.002	4.519	5.005	5.502	6.017	6.510	7.013	
		pH	5.946	6.030	6.121	6.214	6.299	6.389	6.480	6.571	6.675	
15			3.079	3.502	4.000	4.516	5.011	5.500	6.008	6.510	7.017	
			5.964	6.046	6.137	6.231	6.320	6.410	6.504	6.602	6.700	
16			3.001	3.505	4.001	4.500	5.010	5.509	6.001	6.504	7.012	
			5.960	6.058	6.149	6.224	6.299	6.383	6.450	6.569	6.670	
17	20°C		3.070	3.509	4.022	4.510	5.010	5.501	6.010	6.518	7.009	
			5.826	5.911	6.004	6.089	6.176	6.262	6.352	6.451	6.548	
18			3.019	3.502	4.012	4.505	5.041	5.502	6.004	6.500	7.005	
			5.808	5.901	5.996	6.068	6.176	6.259	6.350	6.446	6.546	
19			3.012	3.502	4.010	4.500	5.001	5.503	6.001	6.500	7.040	
			5.801	5.898	5.991	6.075	6.162	6.248	6.340	6.434	6.541	
20	25°C		3.051	3.521	4.005	4.531	5.006	5.501	6.022	6.510	7.007	
			5.697	5.788	5.878	5.969	6.052	6.141	6.238	6.331	6.432	
21			3.015	3.513	4.009	4.631	5.001	5.501	6.020	6.520	7.011	
			5.690	5.788	5.878	5.988	6.050	6.136	6.231	6.329	6.427	
22			3.010	3.502	4.005	4.499	5.052	5.501	6.012	6.500	7.051	
			5.687	5.780	5.873	5.956	6.052	6.130	6.224	6.314	6.425	
23	35°C		3.058	3.501	4.001	4.502	5.015	5.501	6.000	6.510	7.021	
			5.483	5.571	5.661	5.749	5.842	5.926	6.019	6.114	6.219	
24			3.019	3.517	4.012	4.510	5.001	5.500	6.011	6.502	7.005	
			5.489	5.581	5.664	5.743	5.821	5.903	5.996	6.091	6.191	
25			3.001	3.490	4.012	4.529	5.000	5.559	6.082	6.598	7.002	
			5.468	5.566	5.663	5.753	5.834	5.929	6.024	6.122	6.204	

Table 6. Potentiometric titrations of hydroxylamine solutions of ionic strength $I \sim 2.25$ (20°C). 100 ml of solution 0.01 M in $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 2.24 M in NaClO_4 titrated with a 0.09884 M NaOH solution 2.15 M in NaClO_4 . The number of millilitres of NaOH solution added is given above and the pH below.

Titration No.											
26	15°C	ml	3.000	3.500	4.002	4.502	5.000	5.499	6.001	6.499	7.001
		pH	6.053	6.158	6.256	6.343	6.432	6.518	6.611	6.703	6.807
27			3.001	3.500	4.009	4.500	5.015	5.500	6.005	6.505	7.002
			6.062	6.167	6.261	6.343	6.431	6.516	6.605	6.698	6.801
28			3.016	3.521	4.025	4.507	5.010	5.500	6.002	6.520	7.025
			6.049	6.154	6.252	6.340	6.431	6.516	6.606	6.702	6.808
29	20°C		3.009	3.502	4.005	4.501	5.009	5.504	6.010	6.500	7.001
			5.932	6.034	6.132	6.219	6.307	6.393	6.486	6.577	6.677
30			3.022	3.501	4.000	4.502	5.000	5.505	6.000	6.505	7.005
			5.951	6.047	6.140	6.229	6.319	6.405	6.494	6.589	6.690
31			2.996	3.500	4.009	4.519	5.021	5.510	6.004	6.502	7.010
			5.951	6.051	6.149	6.240	6.328	6.413	6.499	6.594	6.697
32	25°C		3.002	3.500	4.000	4.500	5.013	5.510	6.001	6.500	7.000
			5.836	5.932	6.027	6.111	6.201	6.285	6.371	6.464	6.566
33			3.000	3.600	4.000	4.514	5.005	5.500	6.000	6.500	7.005
			5.832	5.950	6.021	6.113	6.197	6.282	6.370	6.463	6.562
34	35°C		3.012	3.501	4.002	4.503	5.001	5.519	6.000	6.501	7.000
			5.617	5.712	5.803	5.893	5.977	6.068	6.152	6.250	6.349
35			3.001	3.501	4.000	4.506	5.001	5.501	6.000	6.500	7.002
			5.617	5.715	5.803	5.893	5.980	6.065	6.152	6.245	6.349

Table 7. Values of pK of hydroxylamine calculated from the data of Table 4.

Titration No.	Temp. °C	pK	Mean pK	I	Mean I	pK (eqn. (6))
1	15	6.214	6.208	0.2455	0.2455	6.214
2		6.197		0.2455		
3		6.214		0.2455		
4		6.094		0.2452		
5	20	6.092	6.092	0.2452	0.2452	6.091
6		6.091		0.2453		
7		5.985		0.2452		
8	25	5.979	5.978	0.2449	0.2450	5.976
9		5.971		0.2450		
10		5.775		0.2442		
11	35	5.759	5.759	0.2442	0.2442	5.758
12		5.744		0.2442		

The experimental results of the potentiometric titrations of hydroxylamine hydrochloride solutions at 15°, 20°, 25°, and 35°C at the ionic strengths 0.25, 1.00, and 2.25 (20°C) are shown in Tables 4–6.

The values of pK calculated on the basis of the data of Tables 4–6 are presented in Tables 7–9. The individual pK values given for each titration

Table 8. Values of pK of hydroxylamine calculated from the data of Table 5.

Titration No.	Temp. °C	pK	Mean pK	I	Mean I	pK (eqn. (6))
13		6.287		0.9961		
14	15	6.306	6.309	0.9961	0.9961	6.300
15		6.329		0.9961		
16		6.314		0.9961		
17		6.184		0.9952		
18	20	6.178	6.178	0.9952	0.9952	6.179
19		6.172		0.9953		
20		6.062		0.9941		
21	25	6.061	6.059	0.9941	0.9941	6.062
22		6.054		0.9942		
23		5.847		0.9910		
24	35	5.838	5.843	0.9910	0.9910	5.845
25		5.843		0.9910		

Table 9. Values of pK of hydroxylamine calculated from the data of Table 6.

Titration No.	Temp. °C	pK	Mean pK	I	Mean I	pK (eqn. (6))
26		6.442		2.2473		
27	15	6.442	6.440	2.2473	2.2473	6.443
28		6.437		2.2473		
29		6.316		2.2453		
30	20	6.328	6.326	2.2453	2.2453	6.326
31		6.334		2.2452		
32	25	6.209	6.208	2.2426	2.2427	6.207
33		6.207		2.2427		
34	35	5.990	5.990	2.2357	2.2357	5.989
35		5.990		2.2357		

series are mean values of eight to nine pK values and the values of pK at each temperature and ionic strength are mean values of eighteen to thirty-six pK values.

The dependence of the value of pK of hydroxylamine on the ionic strength of the solution at each temperature is linear as seen from Fig. 1 and may be represented by the equation

$$pK = pK_0 + BI \quad (6)$$

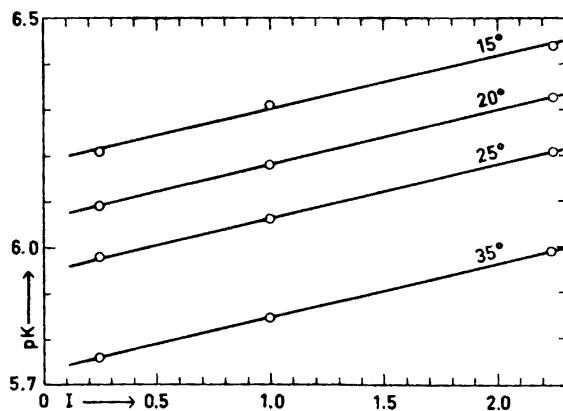


Fig. 1. Values of pK of hydroxylamine as a function of the ionic strength at 15, 20, 25, and 35°C.

where K_0 is the thermodynamic ionization constant and B a constant. The values of the constants of eqn. (6) calculated by the method of least squares on the basis of the mean values of pK given in Tables 7–9 are shown in Table 10.

Table 10. Values of the constants of eqn. (6) calculated by the method of least squares on the basis of the mean values given in Tables 7–9.

Temperature, °C	pK_0	B
15	6.186	0.11475
20	6.063	0.11714
25	5.948	0.11557
35	5.730	0.11621

Table 11. Values of the ionization constant ($K = [\text{NH}_2\text{OH}][\text{H}^+]/[\text{NH}_3\text{OH}^+]$) of hydroxylamine determined at different temperatures by various authors.

Temp. °C	Ionic strength (added salt)	$-\log K$	Method	Ref.
15	0	6.19	gl. elect.	This work
18	0	6.1	conductivity	12
20	0	6.06	gl. elect.	This work
20	0 corrected	6.04	spectrophot.	13
20	0 corrected	6.09	colorimetric	14
20	variable	6.12	conductivity	15
25	0	5.95	gl. elect.	This work
25	variable	5.8	conductivity	16
25	0 corrected	6.60	gl. elect.	17
25	0 corrected	5.98	gl. elect.	18
25	0 corrected	5.96	spectrophot.	13
30	0 corrected	5.84	spectrophot.	13
30	0 variable	6.16	sp., gl. elect.	19
30	variable	6.18	conductivity	15
35	0	5.73	gl. elect.	This work

In Table 11 we have collected values, taken from the literature, of the ionization constant of hydroxylamine at different temperatures. The values in best agreement with values derived in this study are those of Robinson and Bower¹³ and Ölander.¹⁴

Addendum. Szilard (Szilard, I. *Acta Chem. Scand.* **17** (1963) 2674) found by potentiometric titration of dilute hydroxylamine *p*-toluenesulphonic acid salt solutions with a sodium hydroxide solution that the protolysis exponent of hydroxylamine in 0.5 M sodium nitrate at 20°C is 6.12. From eqn. (6) we obtain the value 6.12 for the exponent in 0.5 M sodium perchlorate at 20°C. No greater difference is to be expected between the salt effects of sodium nitrate and sodium perchlorate on the ionization exponent of the hydroxylammonium ion.

C. The thermodynamics of the ionization. The thermodynamic protolysis constants of both hydroxylamine and nitrous acid were assumed to depend on temperature according to the equation²⁰

$$\log K_0 = -(a/T) - cT + b \quad (7)$$

The values of the constants *a*, *b*, and *c* of this equation were calculated by the method of least squares on the basis of the values of pK_0 for the protolytes in Tables 2 and 10. The results are given below:

Protolyte	$a \times 10^{-3}$	<i>b</i>	$c \times 10^3$
Hydroxylamine	2.7757	5.8899	8.4782
Nitrous acid	4.3378	24.125	42.706

In Fig. 2 the negative logarithms of the thermodynamic ionization constants of both protolytes are plotted as functions to the reciprocal of the absolute temperature. The plots seem to be almost linear within the limits of experimental error and show that the acid strengths of both protolytes increase with temperature, that of the weaker acid, hydroxylamine, more rapidly than that of nitrous acid.

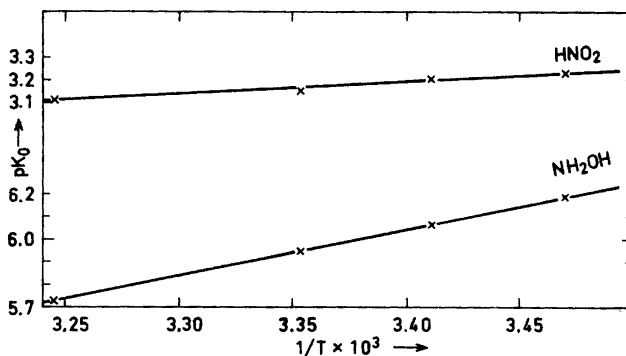


Fig. 2. The negative logarithms of the ionization constants of hydroxylamine and nitrous acid as functions of $1/T$ °K⁻¹. (The lines are arbitrarily drawn to show the deviations from linearity).

Eqn. (7) implies that $-\log K_0$ will have a minimum value at a certain temperature. Both values may be calculated from the constants of eqn. (7) as follows²⁰

$$T_{\min} = (a/c)^{0.5} \quad (8)$$

$$\log K_{0,\min} = b - 2(ac)^{0.5} \quad (9)$$

For hydroxylamine we obtained the values 572°K and -3.81 and for nitrous acid 318°K and -3.09 .

Extensive studies of the protolysis of different acids²¹ have shown that the ionization constants of most acids have maximum values in the range between 0° and 60°C. On the basis of the present study, nitrous acid belongs to this group of acids, whereas the ionization constant of hydroxylamine has its maximum value in the same temperature range as that of water.²²

The changes in the standard free energies, enthalpies, entropies, and heat capacities of the protolytic reactions of both hydroxylamine and nitrous acid were calculated from the equations:

$$\Delta G^\circ = 2.303 R(a - bT + cT^2) \quad (10)$$

$$\Delta H^\circ = 2.303 R(a - cT^2) \quad (11)$$

$$\Delta S^\circ = 2.303 R(b - 2cT) \quad (12)$$

$$\Delta C_p^\circ = -4.606 R c T \quad (13)$$

where $T = 273.16 + t^\circ\text{C}$ and $R = 1.9873 \text{ cal degree}^{-1} \text{ mole}^{-1}$.

Table 12. Thermodynamic data for the protolysis of hydroxylamine in water.

$t^\circ\text{C}$	$\text{p}K_0$ (eqn. (6))	$\text{p}K_0$ (eqn. (7))	ΔG° (kcal)	ΔH° (kcal)	ΔS° (E.U.)	ΔC_p° (cal)	$T\Delta S^\circ$	$T\Delta S^\circ/\Delta G^\circ$ (%)
15	6.186	6.186	8.16	9.5	4.6	-22	1.34	15
20	6.063	6.064	8.14	9.4	4.2	-23	1.26	15
25	5.948	5.947	8.12	9.3	3.8	-23	1.18	15
35	5.730	5.730	8.08	9.0	3.0	-24	0.92	10

Table 13. Thermodynamic data for the protolysis of nitrous acid in water.

$t^\circ\text{C}$	$\text{p}K_0$ (eqn. (2))	$\text{p}K_0$ (eqn. (7))	ΔG° (kcal)	ΔH° (kcal)	ΔS° (E.U.)	ΔC_p° (cal)	$-T\Delta S^\circ$	$-T\Delta S^\circ/\Delta G^\circ$ (%)
15	3.230	3.235	4.27	3.6	-2.2	-113	0.67	15
20	3.203	3.191	4.28	3.1	-4.2	-115	1.18	30
25	3.148	3.157	4.31	2.5	-6.1	-117	1.81	40
35	3.113	3.112	4.39	1.3	-10.0	-121	3.09	70

The calculated values of the thermodynamic quantities are presented for hydroxylamine in Table 12 and for nitrous acid in Table 13.

From these tables we see that ΔH° is positive for both protolytes and hence the ionization reactions are endothermic. The values of ΔH° decrease slightly with increasing temperature.

Table 14. Thermodynamic data for the protolysis of nitrous acid, hydroxylamine and related protolytes at 25°C (unless otherwise stated).

Protolyte	pK_0	ΔG° (kcal)	ΔH° (kcal)	ΔS° (E.U.)	ΔC_p° (cal)	$T\Delta S^\circ$	$ T\Delta S^\circ/\Delta G^\circ $ $\times 100$
HNO ₃	-1.44 ²³	-1.97	-3.30 ²³	-4.46 ²³	-	-1.33	68
HNO ₂	3.15	4.31	2.5	-6.1	-117	-1.81	42
HN ₃	4.72 ²⁴	6.44	3.60 ²⁵	-7.8 ²⁵	-	-2.59	40
HON=NOH	11.54 ²⁶	15.75	8 ²⁶	-26.0	-	-7.75	49
<i>o</i> -ClC ₆ H ₄ .NH ₃ ⁺	2.63 ²⁷	3.59 ²⁸	6.0 ²⁸	8.1 ²⁸	0.0 ²⁸	2.41	67
C ₆ H ₅ .NH ₃ ⁺	4.59	6.27 ²⁸	7.1 ²⁸	2.8 ²⁸	0.0 ²⁸	0.83	13
HONH ₃ ⁺	5.95	8.12	9.3	3.8	-23	1.13	14
NH ₂ .NH ₃ ⁺	7.94 ²⁹	10.83	9.7 ³⁰ (18°)	-3.8	-	-1.13	10
NH ₄ ⁺	9.24 ³¹	12.56 ²⁸	12.38 ³¹	-0.75 ³¹	0 ²⁸	-0.22	2
CH ₃ .NH ₃ ⁺	10.62 ²⁸	14.48 ²⁸	13.09 ²⁸	-4.7 ²⁸	7.5 ²⁸	-1.40	10
(CH ₃) ₂ .NH ₃ ⁺	10.77 ²⁸	14.72 ²⁸	11.88 ²⁸	-9.5 ²⁸	19.9 ²⁸	-2.83	19
(CH ₃) ₃ .NH ⁺	9.80 ²⁸	13.38 ²⁸	8.82 ²⁸	-15.3 ²⁸	41.0 ²⁸	-4.56	34

ΔS° for hydroxylamine is positive and decreases slightly with increasing temperature, whereas the values of ΔS° for nitrous acid are negative, but decrease also with increasing temperature.

The values of ΔC_p° are negative for both protolytes and decrease as the temperature increases. The value found for nitrous acid is rather low, but that for hydroxylamine is of the usual order of magnitude.

The last columns in Tables 12 and 13 give values of the entropy factor as percentages of the values of ΔG° . The percentages show the contribution of

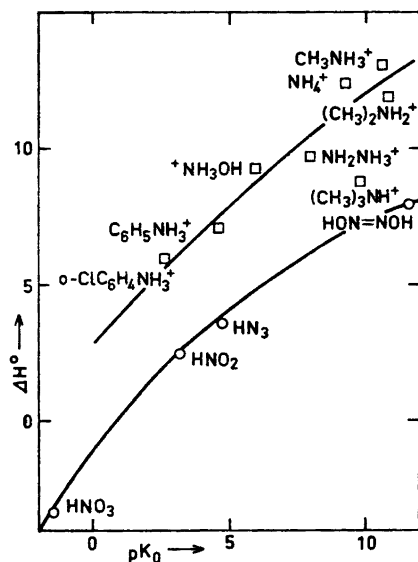


Fig. 3. ΔH° of ionization plotted against pK_0 for hydroxylamine, nitrous acid and related protolytes at 25°C.

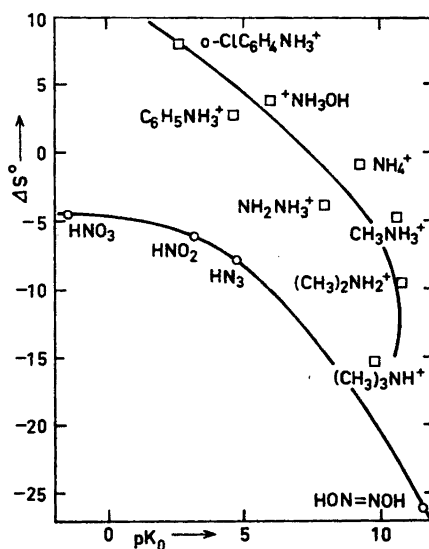


Fig. 4. ΔS° of ionization against pK_0 for hydroxylamine, nitrous acid, and related protolytes at 25°C.

the entropy factor to be small, and hence the enthalpy factor largely determines the ionization of hydroxylamine; both factors are almost constant between 15° and 35°C. In the case of nitrous acid the contribution of the entropy factor increases rapidly with temperature, being already 70 % of ΔG° at 35°C, while the enthalpy factor decreases in value.

Thermodynamic data at 25°C for some protolytes closely related to nitrous acid and hydroxylamine are collected in Table 14. A negative ion is formed in the ionization of the protolytes of the first group, whereas a neutral molecule is formed in the ionization of the protolytes of the second group.

Our knowledge of the values of ΔC_p° of protolytes are imperfect and it is not possible to draw any far-going conclusions from the available data. The reported zero values may, however, change depending on the equation used to express the relationship between the temperature and the ionization exponent.

The curves in Figs. 3—6 are arbitrarily drawn, but show the general dependence between the two quantities. As seen from Figs. 3 and 4, the enthalpy changes increase and the entropy changes decrease with decreasing acid strength of both types of protolyte and the variations are largely similar for both types. The relation between ΔS° and ΔH° shown in Fig. 5 is clear on the basis of Figs. 3 and 4.

When considering the entropy changes in the ionization of ammonium ion and its methyl derivatives, Trotman-Dickenson³² presented the opinion that the decrease of the entropy changes on substituting methyl groups for the hydrogen atoms of ammonia is due to a decreasing power of the nitrogen

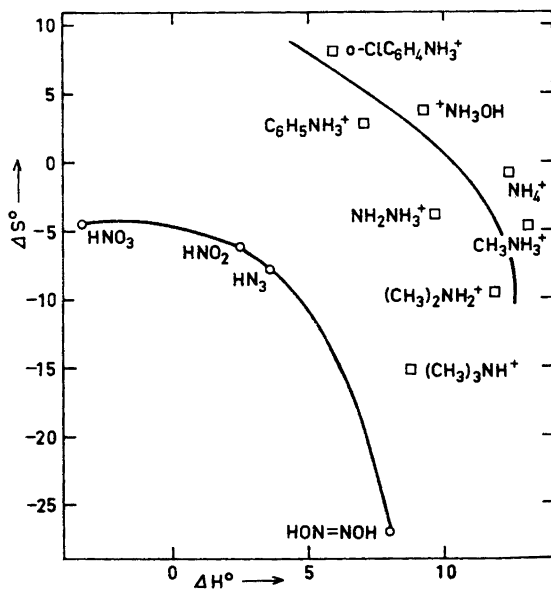


Fig. 5. ΔS° versus ΔH° for the ionization of hydroxylamine, nitrous acid, and related protolytes at 25°C.

atom to form hydrogen bonds with solvent molecules. On the other hand, Evans and Hamann³³ have considered the effect to be due to decreasing solvation on going from the ammonium ion to the trimethylammonium ion.

Our opinion is that both the decrease in the ability to form hydrogen bonds and the degree of solvation may be due to the decrease of the entropy changes and it is difficult, if not impossible, to judge the extent of the effect between them, because the solvation is obviously a consequence of hydrogen bond formation between solute and solvent molecules.

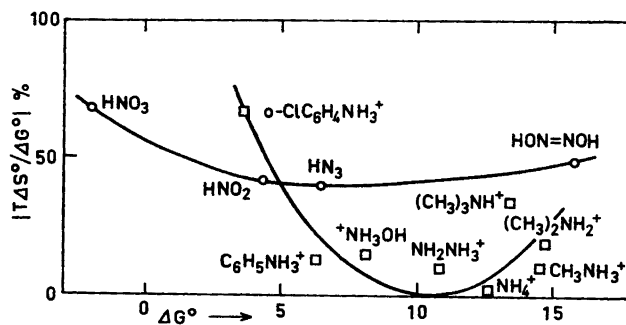


Fig. 6. $|T\Delta S^\circ/\Delta G^\circ|$ % versus ΔG° for the ionization of hydroxylamine, nitrous acid, and related protolytes at 25°C.

In Fig. 6 we have plotted the absolute values of $T\Delta S^\circ/\Delta G^\circ$ in per cent from Table 14 against ΔG° for both protolyte groups under consideration. The entropy factor is a minimum close to zero for the ammonium ion and increases on both sides when the substituents make the protolytes more acidic or basic. This may be connected with the decreasing power of the nitrogen atom to form hydrogen bonds and become solvated (hydrated) on increasing of the substitution. At the same time the contribution of the enthalpy factor decreases from the *o*-chloranilinium to the trimethylammonium ion, but still remains, however, the prominent factor influencing the ionization process.

In the second group of protolytes, the entropy factor is a minimum for nitrous and hydrazoic acids and increases on both sides towards nitric and hyponitrous acids. If the same explanation as above is assumed to be valid, then the nitrous and hydrazoic acids should be most highly solvated and have a greater tendency to form hydrogen bonds with the solvent molecules, although the differences are slight. The contribution of the entropy factor is, however, considerable in this protolyte group; it varies from 40 to 70 % of the value of ΔG° and is almost as large as that of the enthalpy factor.

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