

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Ionization Constant of Hydrazinium Hydroxide¹

BY G. C. WARE, J. B. SPULNIK AND E. C. GILBERT

A systematic investigation of the ionization constant of hydrazinium hydroxide ("hydrazine hydrate"), its variation with temperature and with ionic strength, has never been reported. Bredig² measured the conductivity of aqueous solutions of hydrazine and calculated the ionization constant at 25°. He reported some difficulty due to decomposition and his values varied from 4.4 to 2.2×10^{-6} depending upon the concentration. The mean of these two, 3×10^{-6} , is the value commonly accepted and used in text and reference works, although the "International Critical Tables"³ accepts the lower value 2.2×10^{-6} . Hughes using the glass electrode made a single measurement⁴ and reported a value of $1.4-1.7 \times 10^{-6}$ depending upon the interpretation of his results. Gilbert studied the equilibrium⁵ between ammonia and hydrazine in aqueous solutions and obtained the ratio of the constants of the two bases at 20° and two ionic strengths. The method is not suitable for extension to a general study at various temperatures and concentrations such as made in the present investigation.

The work described in this paper was carried out by the use of the glass electrode. The highly reactive nature of hydrazine and its instability in the presence of platinum black makes it impossible to use the quinhydrone or hydrogen electrode satisfactorily. Furthermore, it is impossible for the same reason to use the ordinary reference electrodes (calomel, mercuric oxide, or silver chloride) except through the medium of a liquid junction or salt bridge. However, the recent important work of Guggenheim and Schindler⁶ on cells with liquid junction justifies confidence in this type of measurement within certain limits. The method has moreover been applied recently for a similar study of hypochlorous acid.⁷

Experimental Part

The hydrogen ion activity of a series of solutions was

(1) A portion of this paper is taken from a thesis submitted by J. B. Spulnik for the degree of Master of Science in June, 1935, at the Oregon State College.

(2) Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

(3) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, Vol. VI, p. 260.

(4) Hughes, *J. Chem. Soc.*, 491 (1928).

(5) Gilbert, *J. Phys. Chem.*, **33**, 1236 (1929).

(6) Guggenheim and Schindler, *ibid.*, **38**, 533 (1934).

(7) Ingham and Morrison, *J. Chem. Soc.*, 1200 (1933).

determined, each containing exactly equivalent amounts of hydrazinium hydroxide and hydrazinium ion, the ionic strength being varied by the addition of potassium sulfate, sodium chloride or sodium perchlorate. Measurements were made at 15, 25 and 35°, using a vacuum tube potentiometer of the type devised by De Eds.⁸ Considerably more shielding was found advisable than specified by De Eds. The following cell arrangement was used

Hg, Hg₂Cl₂, KCl (0.1 N) | KCl (satd.) | unknown solution, glass, buffer | KCl (0.1 N), Hg₂Cl₂, Hg

When a reading had been made with the "Unknown Solution" in the cell, this was replaced with a buffer of similar ionic strength whose hydrogen ion activity had been determined accurately by the use of a hydrogen electrode at the same temperature. From these quantities the hydrogen ion activity of the hydrazinium buffer may be calculated readily.⁹ Voltage readings could be duplicated within 0.3-0.5 mv., corresponding to ± 0.01 pH. Calculation of the liquid junction potentials by Henderson's formula¹⁰ as recommended by Guggenheim and Schindler showed them to be less than the uncertainty in the voltage readings. The liquid junction was made with the type of salt bridge devised by Ingham and Morrison,⁷ which proved to be highly reproducible if subject to careful temperature control. In measuring the pH of the standard buffers with the hydrogen electrode the value given by Guggenheim and Schindler,⁶ 333.7 mv., was used for the 0.1 N calomel electrode at 25°, 334.2 at 15° and 332.9 at 35°.

The solutions were made by weight, adding the calculated amount of carbonate-free sodium hydroxide solution to hydrazinium perchlorate solutions or in one series by adding barium hydroxide to hydrazine sulfate. The barium hydroxide was standardized gravimetrically. The ionic strength was adjusted by the addition of neutral salts such as potassium sulfate, sodium chloride or perchlorate. The water was de-oxygenated and the solutions were protected from the atmosphere at all times. Readings were constant with the glass electrode and easily duplicated.

Results

In Table I are given the results of the measurements. At each temperature determinations were made at a series of salt concentrations permitting extrapolation to zero ionic strength. The measurements at 25° were repeated with different salts. In agreement with Brönsted's principle of specific ionic interaction the slopes of the curves for different salts were different but extrapolation led to the same value at zero ionic strength. The rather small salt effect observed

(8) De Eds, *Science*, **78**, 556 (1933).

(9) Cobb and Gilbert, *Ind. Eng. Chem., Anal. Ed.*, **5**, 69 (1933).

(10) Henderson, *Z. physik. Chem.*, **69**, 118 (1907); **63**, 325 (1908).

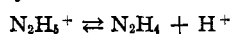
agrees with the predictions of Brönsted's extended theory of acids and bases, namely, that for bases of the ammonia type the dissociation constant should be little affected by salts.¹¹

TABLE I
HYDROGEN ION ACTIVITY OF HYDRAZINIUM BUFFER SOLUTIONS^a

μ (total)	(a) In presence of K_2SO_4		
	15°	25°	35°
0.000	8.24	7.99	7.82
.009	8.25	7.99	7.82
.029	8.24	7.99	7.82
.044	8.27	...	7.83
.095	8.30	8.02	7.87
.170	8.37	8.09	7.90
μ (total)	(b) In presence of NaCl		
	25°		
0.000	7.99		
.010	7.99		
.050	8.00		
.100	8.02		
.150	8.04		
μ (total)	(c) In presence of $NaClO_4$		
	25°		
0.000	8.00		
.010	8.00		
.050	8.01		
.100	8.02		
.150	8.03		

^a Expressed as pH .

Since the experimentally determined quantity in this work is the hydrogen ion activity, the calculations follow more simply if made on the basis of treating the hydrazinium ion as an acid.



then

$$\frac{(a_{N_2H_4}a_{H^+})}{a_{N_2H_5^+}} = K_A$$

and

$$pK_A = pH + \log(a_{N_2H_5^+}/a_{N_2H_4})$$

At zero ionic strength where $a_{N_2H_5^+} = m_{N_2H_5^+}$ and in an equimolal solution of N_2H_4 and $N_2H_5^+$

(11) Brönsted, *Chem. Rev.*, **5**, 281 (1928).

such as used in this work pK_A may be taken as equal to pH .

Values for K_A obtained in this manner are shown in Table II. Now from the ion product of water as recently accurately determined by Harned and Hamer¹² the corresponding conventional ionization constant of the hydrazinium hydroxide may be calculated since $K_B = K_w/K_A$. These values are also shown in Table II, together with the corresponding values for ΔF° for the basic ionization. The value for $\Delta H_{291.1}$ calculated from these results is 3850 cal., which may be compared to the value 3950 cal. obtained calorimetrically by Bach.¹³ This quantity has a very large temperature coefficient. Since different salts affect the ionization constant to a different degree, it is not possible to set up a general equation for the constant as a function of the ionic strength. The observed salt effect however is not large.

TABLE II
IONIZATION CONSTANT OF HYDRAZINIUM ION AS AN ACID, AND OF HYDRAZINIUM HYDROXIDE AS A BASE

	15°	25°	35°
$K_A \times 10^9$	5.75	10.2	15.2
$K_B \times 10^6$	0.785	0.984	1.37
ΔF° , cal.	8052	8200	8270

The values which have been found are considerably lower than those commonly accepted. They are of course the extrapolated values as opposed to those which have previously been determined in the presence of salts.

Summary

The ionization constants for the hydrazinium ion as an acid and hydrazinium hydroxide as a base have been determined at 15, 25 and 35° from glass electrode measurements.

CORVALLIS, OREGON

RECEIVED JUNE 22, 1936

(12) Harned and Hamer, *THIS JOURNAL*, **55**, 2194 (1933).

(13) Bach, *Z. physik. Chem.*, **9**, 241 (1892).