which can compete for the metal ion, there results a competitive reaction which can reduce the concentration of the actual complex required for the hydrolysis.[3] Cysteine methyl ester is an example of this type of inhibition of the ester hydrolysis. The strong affinity of the sulfhydryl group for the metal ion results in a complex (IV) which is much more stable than the complex (III) required for the hydrolysis.

Other amino acid esters which are capable of reacting with the metal ion in a manner other than that indicated for glycine are histidine, tyrosine and aspartic acid.

Glutamic acid dimethyl ester was found to undergo a relatively rapid conversion to the methyl ester of pyrrolidone carboxylic acid. The addition of cobaltous ion accelerated the rate of breakdown of the dimethyl ester so that the over-all effect resulted in an observed first order constant 1.1 times greater than found with glycine methyl ester.

NEW HAVEN, CONN. RECEIVED MAY 25, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

An Acidity Function in Aqueous Hydrazine[1]

BY N. C. DENO

An acidity function (H_-) has been determined from 5–60% (by weight) hydrazine by the use of indicators. This function is identical with pH (measured by the glass electrode) from pH 11 to 12, and reaches the value 15.93 in 60% hydrazine. This H_- function is used to establish a scale of pK values for weak acids.

Hammett[2–4] showed that an acidity function defined by equation (1) could be determined in media whose acidities were outside the pH range in water.

$$H = -\log a_{H^+} - \log f_B/f_{HB} \qquad (1)$$

It was necessary to the success of this acidity function that the term $\log f_B/f_{HB}$ be independent of the indicator used. Hammett found this to be true in sulfuric acid–water mixtures providing indicators of a single charge type were employed.

It was the purpose of the present work to extend Hammett's concept of an acidity function into strongly basic media. Such a function would be of use in determining the relative strengths of weak acids, and with certain base-catalyzed reactions, it should bear a linear relationship to the log of the rate constant. This would be analogous to the linear relationship between H_0 and $\log k$ which Hammett[4] and others[5] have found for certain acid-catalyzed reactions.

A series of neutral weak acids were chosen as indicators. Using Hammett's notation, this acidity function is an H_- function and would be defined by equation (2). The indicators would react as in equation (3).

$$H_- = pK_{HA} + \log c_{A^-}/c_{HA} = -\log a_{H^+} - \log f_{A^-}/f_{HA} \qquad (2)$$

$$A^- + H^+ = HA \qquad (3)$$

Experimental

All spectral measurements were made by means of a Beckman model DU spectrophotometer. With each indicator the spectrum above 400 mμ was recorded for anion and neutral acid. The principal absorption maxima of the anions were chosen as the wave lengths to measure c_{A^-}/c_{HA}. This decreased the error due to the change in spectrum with changing media. With all indicators except number VIII, the absorption of the neutral indicator was zero at the wave length employed. The maxima, log e, and slit widths employed are given in Table II.

It was assumed that all indicators ionized according to equation 3 except indicator VIII. Indicator VIII belongs to the charge type $A^=$ since its first acidic hydrogen is known to ionize at a much lower pH. The acidity function defined by VIII would be an $H_=$ function. It is remarkable that this $H_=$ acidity function defined by VIII follows so closely the H_- function given in Table I.

Stock acetone solutions were used to introduce the indicators. One or two drops of the acetone solution (concentration about 0.2%) were added to the hydrazine solution. This provided a rapid method of dispersing the indicators into the solution. Since most of the indicators slowly reacted with hydrazine, this rapid dispersal was necessary. With p-nitrobenzyl cyanide (indicator I), an ethanol solution was used in hydrazine concentrations below 20%. Although acetone reacts with hydrazine, it is believed that the amount added, 0.02 g. per 10 g. of hydrazine solution, had a negligible effect on the basicity of the media.

3,6-Dinitrocarbazole (II).—The carbazole to be nitrated was prepared by the method of Horning[6] to ensure absence of other aromatic compounds. Nitration was effected with 70% nitric acid in acetic acid.[7] The m.p. has been reported as 320°.[7] The initial product does melt around 320°, but after vacuum sublimation and several crystallizations from nitrobenzene, the fine needles melt at least above 340° and retain only a cream color (previously gold to brown).

1- and 3-Nitrocarbazole.—The procedure of Morgan and Mitchell[8] was used. The small amount of 1-nitrocarbazole is easily separated by their procedure. However, the 3-nitrocarbazole, which was implied to be the major product and easily obtainable, was impure. After considerable recrystallization only a small amount was finally obtained in fairly pure form.

Discussion

The system hydrazine–water was chosen for the following reasons.[9] Hydrazine is basic and is unique in possessing a m.p. (2°), b.p. (117°), and dielectric constant (ϵ = 53 at 20°),[10] close to the values of the same properties for water. This similarity in dielectric constant is particularly advantageous since in going from pure water to pure hydrazine there will be relatively small changes in a large dielectric constant. This circumstance should

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[1] This work was performed under Contract AF33(038)-20391 between The Pennsylvania State College and the Office of Air Research.

[2] L. P. Hammett, THIS JOURNAL, **50**, 2666 (1928).

[3] L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).

[4] L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

[5] N. C. Deno and M. S. Newman, *ibid.*, **72**, 3852 (1950).

[6] E. C. Horning, M. G. Horning and G. W. Walker, *ibid.*, **70**, 3935 (1948).

[7] P. Ziersch, *Ber.*, **42**, 3799 (1909).

[8] G. T. Morgan and J. G. Mitchell, *J. Chem. Soc.*, **3283** (1931).

[9] The author is indebted to Dr. W. C. Fernelius for suggesting the use of hydrazine in these studies.

[10] H. Ulich and W. Nespital, *Z. physik. Chem.*, **16B**, 221 (1932).

contribute to the constancy of log f_{A^-}/f_{HA} with changing hydrazine concentration, and thus make the acidity function more independent of indicator.

There has been one previous attempt to determine an acidity function in strongly basic media.[11] Concentrated sodium and potassium hydroxide solutions were studied. The indicators used were not employed in this investigation and so the results at present cannot be compared.

The values of H_- at hydrazine concentrations from 5–60% are recorded in Table I. These values were calculated from the data in Table II. The graphs of log c_{A^-}/c_{HA} against % hydrazine were linear above 20% hydrazine which facilitated the drawing of smooth curves. Even from 5–20% hydrazine the deviation from linearity was small. This linearity also aided the fitting of curves so that the curve of one indicator was contiguous and/or congruent with that of the next indicator in the series. The precision can be seen by comparing the average values in Table I with the individual values in Table II. By appropriately fitting these curves it was possible to keep the deviations to within 0.1 H_- unit.

The results appear in a form easily remembered. Each 10% increase in hydrazine concentration causes an increase of about one unit in H_-. By extrapolation one can estimate that H_- in 90% hy-

TABLE I

H_- AT 5-60% HYDRAZINE

Hydrazine, %	H_-[a]	pH[b]
5	11.18	11.18
10	11.55	11.55
15	11.93	11.93
20	12.29	
25	12.72	
30	13.15	
35	13.56	
40	14.03	
45	14.52	
50	14.99	
55	15.43	
60	15.93	

[a] These are average values derived from the curves of the indicators applicable at each concentration. [b] These are calculated from a curve of pH against % hydrazine concentration. The pH was measured by means of a glass electrode designed for use in alkaline media.

TABLE II

LOG c_{A^-}/c_{HA} *vs.* % HYDRAZINE

p-Nitrobenzylcyanide (I); pK 13.43; measurements made at 535 mμ with 0.4-mm. slit width; log e 4.346; curve equated to pH from pH 11 to 12

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
5.0	−2.24	11.19
10.2	−1.88	11.55
15.2	−1.46	11.97
20.2	−1.18	12.25
22.7	−0.95	12.48
25.6	− .64	12.79
30.1	− .29	13.04
33.2	− .04	13.39
36.5	.28	13.71
40.4	.57	14.00

3,6-Dinitrocarbazole (II); pK 13.07; measurements made at 492 mμ with 0.5-mm. slit width; log e 4.357; curve equated to curve of I at 30% hydrazine

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
17.5	−1.05	12.02
20.2	−0.82	12.25
25.3	− .29	12.78
30.5	.09	13.16
33.2	.42	13.49
36.7	.74	13.81

3-Nitrocarbazole (III); pK 14.16; measurements made at 492 mμ with 0.5-mm. slit width; log e 4.143; curve equated to curve of II at 40% hydrazine

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
40.9	0.01	14.17
43.9	.26	14.42
45.2	.37	14.53
46.4	.43	14.59
50.3	.81	14.97
53.1	1.09	15.25

4,4′-Dinitrodiphenylamine (IV); pK 14.48; measurements made at 595 mμ with 0.5-mm. slit width; log e 4.590; curve equated to curve of III at 45% hydrazine

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
33.2	−1.18	13.30
35.6	−0.92	13.56
40.3	− .51	13.97
44.2	.00	14.48
50.1	.55	15.03
52.6	.80	15.28

4-Nitrodiphenylamine (V); pK 15.43; measurements made at 500 mμ with 0.5-mm. slit width; log e 4.460; curve equated to curve of III at 50% hydrazine

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
48.6	−0.59	14.84
51.7	− .31	15.12
54.8	.01	15.44
56.5	.14	15.57
59.9	.50	15.93

4,4′-Dinitrodiphenylmethane (VI); pK 15.90; measurements made at 570 mμ with 0.5-mm. slit width; log e 4.66

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
50.2	−0.86	(15.04)
59.8	.03	(15.93)

4,4′,4″-Trinitrotriphenylmethane (VII); pK 14.67; measurements made at 650 mμ with minimum slit width; log e 4.3

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
33.2	−1.07	(13.60)
50.2	0.33	(15.00)
59.8	1.0	(15.67)

4-(p-Nitrophenylazo)-resorcinol (VIII)[a]; pK 11.93; measurements made at 580 mμ with 0.5-mm. slit width; log e 4.460; curve equated to pH at pH 11.90

Hydrazine, %	log c_{A^-}/c_{HA}	H_-
3.0	−1.16	10.87
6.0	−0.60	11.33
9.1	− .34	11.59
13.0	− .15	11.80
15.5	− .03	11.96
18.1	.31	12.24
21.8	.51	12.44

[a] The log e at 580 mμ was unchanged from 30–40% hydrazine. However, there was about a 20% increase in log e at 580 mμ in going from 40–60% hydrazine. Although this indicator belongs to a different charge type ($A^- + H^+ \rightarrow HA^-$), the H- values (actually $H_=$ values) agree with the H- values in Table I.

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[11] G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1944).

drazine should be about 19. From 90–100% hydrazine a much more rapid rise in H_- is anticipated corresponding to the rapid increase in *p*H from 0–5% hydrazine.

There have been several estimates of pK values for weak acids. The most extensive were based on acid–base equilibria in ether.[12] The pK values measured in hydrazine reach, but do not overlap, those measured in ether.

By spectral measurements in dilute aqueous alkali,[13] the pK of *p*-nitrobenzyl cyanide was measured to be 13.4. This is in agreement with the value in Table II (13.43). It is of interest to compare the values of pK derived from spectral measurements in ethanol solution with those measured in aqueous hydrazine: 4-nitrodiphenylamine, pK 20.6 (ref. 8) compared with 15.43 (Table II); trinitrotriphenylmethane, pK 17.44 (ref. 13 and 14) with 14.7 (Table II).

Although 4,4′-dinitrodiphenylmethane (VI) and 4,4′,4″-trinitrotriphenylmethane (VII) were not used as indicators, approximate pK values were determined. With VI it was not certain that the indicator was completely ionized in 66% hydrazine, the highest concentration employed. With VII the color was fleeting so that only approximate measurements could be made. Both VI and VII gave about the same rate of change of H_- with hydrazine concentration as indicators I–V, and are assumed to ionize according to equation (3).

Of the indicators employed, only VI and VII showed a measurable time lag before complete development of color (about 4 minutes with VI and 30 seconds with VII). This agrees with previous observations that the rate of removal of the proton from carbon, in contrast to oxygen and nitrogen, is frequently measurably slow.[14,15] Visually both VI and VII change from colorless in dilute hydrazine to deep blue in 66% hydrazine. In contrast *p*-nitrotoluene fails to show any detectable color in 66% hydrazine.

Bis- and tris-(2,4-dinitrophenyl)-methane gave momentary blue colors at certain hydrazine concentrations, but the colors changed in a matter of seconds to an orange. The orange colored compound failed to act as an indicator in the region studied.

The pK of 1-nitrocarbazole was too high to measure, but it was determined to be greater than 16. Thus a large difference in acidity exists between 1- and 3-nitrocarbazole.

Several diphenylamines and carbazoles containing 2,4-dinitro substitutents were unsatisfactory because the colors were unstable. N-(4′-Nitrophenylazo)-4-nitroaniline was arbitrarily discarded because the data gave a different rate of change of H_- than did the other indicators.

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[12] J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).

[13] R. S. Stearns and G. W. Wheland, *ibid.*, **69**, 2025 (1947).

[14] G. N. Lewis and G. T. Seaborg, *ibid.*, **61**, 1894 (1939).

[15] R. G. Pearson, *ibid.*, **70**, 204 (1948); R. G. Pearson and J. M. Mills, *ibid.*, **72**, 1692 (1950).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of Quartz and Cristobalite

BY G. L. HUMPHREY AND E. G. KING

A combination of combustion and solution calorimetry was used to obtain the heats of formation of low-quartz and low-cristobalite from the elements. The results are $\Delta H_{298.16} = -210{,}260 \pm 270$ and $\Delta H_{298.16} = -209{,}330 \pm 250$ cal./mole.

In connection with work on some thermodynamic properties of silicon carbide, we had cause to determine the heats of formation of low-quartz and low-cristobalite. The values obtained differ from those in the literature and also are more precise. A combination of combustion and solution calorimetry was employed in determining the heat of formation of low-cristobalite. Heat of solution measurements served to obtain the heat of transformation of low-cristobalite to low-quartz.

Materials.—The crystalline silicon for the combustion calorimetry was 99.81% pure, according to the manufacturer. The major metallic impurities were determined by spectrographic analysis[1] to be (in %): Mg, 0.007; Al, 0.03; Cu, 0.0025; Ca, 0.02; Cr, 0.005; Ni, 0.002; Ti, 0.0005; and Fe, 0.007. The silicon was ground to -325 mesh with a boron carbide mortar and pestle, and stored in a desiccator containing Dehydrite.

The sample of low-cristobalite, used in the heat of solution measurements, was prepared in this Laboratory[2] from pure quartz (99.9% SiO_2), by prolonged heating at 1480 to 1500°. The X-ray diffraction pattern showed only lines of low-cristobalite, there being no evidence of any untransformed quartz.

Measurements.—The heat of combustion of silicon was determined in apparatus described[3] previously. The energy equivalent of the calorimeter was obtained as 32,384.8 cal./ohm with an average deviation of ±0.02% by combustion of National Bureau of Standards benzoic acid, Standard Sample 39 g. As it was necessary to carry out the calorimetric combustions of silicon under conditions somewhat different than those for the calibration experiments, the energy equivalent was corrected accordingly for each combustion. These corrections averaged 0.06%.

The combustions of silicon were made in silica-glass crucibles that were heavily lined with pure rutile and strongly ignited. (Quartz and cristobalite linings were tried, but their use was precluded by the glassy character of the combustion products.) The oxygen pressure for combustion was 40 atm., and no water was added to the bomb. Samples were ignited by a filter paper fuse without the aid of any kindler. The average size of silicon sample was 0.368 g. mass *in vacuo*. Combustions of the silicon were on the average about 99.9% complete, as determined by strong ignition to constant weight in air of the combustion products. Corrections were applied to the individual heat of combustion

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[1] We are indebted to G. M. Gordon, Division of Mineral Technology, University of California, for this analysis.

[2] We are indebted to R. E. Lorenson for the preparation and testing of this material.

[3] G. L. Humphrey, THIS JOURNAL, **73**, 1587 (1951).