Summary

1. The equilibria in the adsorption system hydrogen/outgassed tungsten powder, the measurement of which was described in a previous paper, are discussed, in relation to the general theories of the adsorption of gases on metallic surfaces.

2. It is shown that a theoretical derivation of the measured adsorption equilibria can be based on Langmuir's formula for adsorption isotherms with the modification that the latter formula has to be adapted to the rapid decrease of the differential heats of adsorption with increasing covering of the tungsten surface with adsorbed hydrogen.

3. A detailed discussion of the slopes of the experimental "logarithmic isotherms," in combination with the theory underlying Langmuir's formula, leads to the evaluation of the saturation value S of the adsorption (1 adsorbed hydrogen molecule per two tungsten atoms in the surface), and to the conclusion that the adsorbed hydrogen exists on the surface in form of atoms, at all surface coverings $<0.008\ S$, and as "molecules," at all surface coverings $>0.008\ S$.

4. Q, the differential heat of adsorption of the hydrogen molecules, decreases, at a given temperature, according to $Q = C - c \log A$ (A = adsorbed amount). It is further temperature independent, for a given surface covering, from low temperatures up to 529°; at temperatures above 529° a sharp decrease with increasing temperatures takes place.

5. These changes of the heats of adsorption with surface covering and temperature can be explained by either a very heterogeneous nature of at least 40% of the total surface of the tungsten powders (corresponding to a "frozen Maxwell equilibrium" of the surface tungsten atoms), or by the assumption that the adsorbed hydrogen molecules exist on the tungsten surface in different states, varying from a widely stretched configuration, at low concentrations of the adsorbed phase, to molecules with the normal H–H distance, at coverings close to saturation. The forces between two widely separated hydrogen atoms of the stretched adsorbed molecules are, according to this picture, due to the fact that clouds of electrons of the adsorbent metal participate as components of the adsorption complex hydrogen–tungsten. Whereas these clouds attract the hydrogen atoms as independent units, as long as the atoms are widely separated, they start to overlap each other as soon as the distance of the adsorbed hydrogen atoms falls below a certain value. The electrons of the overlapping clouds which are shared by two adjacent hydrogen atoms, act as binding electrons, bringing about a kind of molecular bond between the two hydrogen atoms. This hypothetical picture leads, under simple quantitative assumptions, to a variation of the heats of adsorption which is in agreement with the experiment, and seems to provide an explanation for the sharp drop of the heats of adsorption, at temperatures above 529°.

6. A decision in favor of this picture, against the explanation based on a heterogeneous nature of the tungsten surface, requires further experimental work with tungsten surfaces of widely different structures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Ionization Constants of Butylamine, Piperidine and Triethylamine in Methanol

BY JOHN R. SCHAEFGEN, MELVIN S. NEWMAN AND FRANK H. VERHOEK

The concentration ionization constants of butylamine, piperidine, and triethylamine in methanol were determined in connection with an investigation of the methanolysis of pseudo *l*-menthyl *l*-*o*-benzoylbenzoate.[1] The procedure used involved (a) the determination of the concentration ionization constants, K_A, of the conjugate acids of the amines by the method of Kolthoff and Guss,[2] using brom cresol purple as the indicator; and (b) a conversion of these values of K_A to the basic concentration ionization constants, K_B, by use of the ion product constant of methanol.

Procedure and Materials.—The protolysis equilibrium measured may be written

$$B + HIn^- \rightleftharpoons BH^+ + In^=$$

where HIn^- represents the acid form of brom cresol purple and $In^=$ the basic. The maximum absorption of the basic form in methanol occurs at 583 mμ.[3] Solutions of amine, amine salt, and indicator were mixed and the absorption of the resulting solution at 583 mμ was determined with a Beckmann Quartz Spectrophotometer. If the amine and amine salt solutions were mixed first and the indicator solution added, the absorption was found to decrease slowly with time. If the three solutions were mixed at the same time the absorption increased to a maximum in five to ten minutes and then decreased very slowly. The magnitude of this change in an experiment with $1.28 \times 10^{-3}\ M$ butylamine and $5.67 \times 10^{-3}\ M$ butylammonium ion was as follows: after 3.6, 5.6, 9.0, and 12.4 minutes the extinction was 1.271, 1.275, 1.267, 1.264. Values of the protolysis constant K, obtained by extrapolating to zero time, when the indicator was added after the amine buffer had come to equilibrium, and those values obtained by using the maxi-

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[1] Schaefgen, Newman and Verhoek, forthcoming publication in THIS JOURNAL.

[2] Kolthoff and Guss, THIS JOURNAL, **60**, 2516 (1938).

[3] The absorption maximum for the acid form occurs at 417 mμ; the isobestic point at 476.5 mμ. See Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, p. 249.

mum value of the extinction when all constituents were mixed simultaneously gave identical results within the limits of error.[4] In most experiments the second procedure was used in calculating the values of the protolysis constants, K. Since the absorption of the acid form of the indicator is zero at 583 mμ, the measured extinction is proportional to the amount of indicator in the basic form.[5]

The absorption of the totally basic form at the same indicator concentration and the same salt concentration as in the unknowns was determined by measuring the absorption of a methanol solution of indicator and sodium methylate, to which various amounts of sodium chloride had been added. The fraction of indicator in the acid form I_A was taken as $1 - I_B$.

All measurements were made at room temperature (30 ± 2°).

Methanol.—A C. P. acetone-free product was dried over magnesium methylate,[6] and then distilled from this reagent through a column packed with glass helices and equipped with a total reflux partial takeoff head. Only freshly distilled product was used in making up solutions.

Brom cresol purple was recrystallized twice from glacial acetic acid, and dried in a vacuum at 100°. It was used as the free acid, and the concentrations of amine and amine salt were corrected for the amount of amine that reacted with the indicator.

Amines.—The best Eastman Kodak Co. products were shaken over barium oxide and then distilled through a packed column, retaining the middle constant-boiling fraction.

Salts.—The amine salts, piperidinium *p*-toluenesulfonate, butyl-ammonium benzenesulfonate, and triethylammonium benzenesulfonate were prepared by mixing ethyl acetate solutions of the amine and the appropriate acid, and recrystallizing the resulting salt from ethyl acetate–ethanol. Reagent grade sodium chloride was used. All salts were dried in a vacuum at 100° before use.

Solutions.—Methanolic solutions of the amines were standardized by titration. The salt solutions were made up by weight. Dilution of these original solutions was carried out with calibrated pipets.

According to the Debye–Hückel theory the activity coefficient of an ion in methanol is given by the equation: $\log f_i = -2.0 z^2 \sqrt{\mu}$. Using this equation, the relationship between the protolysis constant and the ionic strength for the neutral base and univalent anion indicator becomes: $pK' = pK + 8.0 \sqrt{\mu}$ (K' is the thermodynamic protolysis constant). A graph of pK against the square root of the ionic strength was found to be a straight line in dilute solution ($\sqrt{\mu} < 0.10$) with the following observed slopes: butylamine, −8.3; piperidine, −8.4; triethylamine, −12.6.

The experimentally determined protolysis constant K is related to K_A and K_I, the concentration ionization constant of the indicator, by the equation: $pK_I = pK + pK_A$. Values of pK_I at various ionic strengths are available in the literature,[7] so that pK_A may be calculated.

The basic concentration constants (K_B) were calculated from K_A using values of the ion product constant of methanol (K_m) taken from the data of Buckley and Hartley,[8] and Bjerrum, Unmack and Zechmeister.[9]

At 25°	μ	0.00	0.01	0.0217	0.0626
	pK_m	16.71	16.48	16.34	16.18

The last two values at higher ionic strengths were calculated from the data of Buckley and Hartley, using their values for the activity coefficient of an ion at the concentration in question. Graphical interpolation gave intermediate values of pK_m. The basic ionization constant is related to the ionic strength by the equation $pK_B' = pK_B + 4.0 \sqrt{\mu}$. The slopes observed for pK_B as a function of $\sqrt{\mu}$ were: butylamine, −4.3; piperidine, −4.8; triethylamine, −7.6.

Values of pK, pK_A, pK_B are given in Table I, together with the equilibrium concentrations of amine and ammonium ion and the ionic strength. The values of pK_A for butylamine at higher ionic strengths (pK_A = 11.75 to 11.78) are in excellent agreement with the values determined by Goodhue and Hixon[10] from electromotive force data (pK_A = 11.78 to 11.79). The thermodynamic basic ionization constant at zero ionic strength determined in

TABLE I

VALUES OF pK, pK_A, AND pK_B FOR BUTYLAMINE, PIPERIDINE, AND TRIETHYLAMINE IN METHANOL AT ROOM TEMPERATURE

Amine-H+, m./l. × 10^3	Amine, m./l. × 10^3	$\mu \times 10^3$	pK	pK_A	pK_B
Butylamine (brom cresol purple, 2.8 × 10^{-5} M)					
		0.000	−0.34	11.64	5.07
0.270	0.611	.293	− .47	11.66	5.01
.705	.613	.726	− .57	11.70	4.94
1.17	.615	1.19	− .63	11.70	4.93
5.67	1.28	5.69	− .96	11.78	4.75
12.6	2.31[a]	12.6′	−1.14	11.77	4.67
25.7	2.31[a]	25.7	−1.33	11.75	4.58
28.8	2.59	28.8	−1.38	11.75	4.56
Piperidine (brom cresol purple, 2.8 × 10^{-5} M)					
		0.000	−0.27	11.57	5.14
0.151	0.416	.173	− .40	11.61	5.07
.250	.418	.270	− .39	11.59	5.08
.351	.418	.371	− .46	11.64	5.02
.446	.420	.464	− .42	11.58	5.08
1.19	.99[b]	1.21	− .58	11.65	4.98
9.97	1.79	9.99	−1.12	11.81	4.66
25.5	3.61	25.5	−1.39	11.81	4.52
Triethylamine (brom cresol purple, 2.8 × 10^{-5} M)					
		0.000	0.59	10.71	6.00
0.150	0.69	.163	.49	10.72	5.96
.146	.834	.171	.44	10.77	5.91
.563	3.44	.583	.24	10.91	5.74
1.05	4.43	1.07	.21	10.88	5.75
2.04	22.3	2.06	.05	10.96	5.64

[a] Indicator concentration 2.5 × 10^{-5} M.
[b] Indicator concentration 3.1 × 10^{-5} M.

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[4] Ogston, *J. Chem. Soc.*, 1022 (1936), has suggested that ionization of amines in methanolic solution is a slow process. This may be the explanation for the initial increase in extinction. The slow decrease remains unexplained.

[5] Brode, THIS JOURNAL, **46**, 581 (1924).

[6] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

[7] Kolthoff and Guss, THIS JOURNAL, **61**, 330 (1939).

[8] Buckley and Hartley, *Phil. Mag.*, **78**, 320 (1929).

[9] Bjerrum, Unmack, and Zechmeister, *Kgl. Danske Videnskab Selskab. Math.-fys. Medd.*, **5**, 11 (1924).

[10] Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934).

this work differs somewhat from their value because of the small change of pK_A with ionic strength.

Comparison of the thermodynamic ionization constants at zero ionic strength for the three amines with the corresponding values in water[11] gives the following values for the difference in the logarithmic constants, $\Delta pK'_B$, in the two media: butylamine, 1.68; piperidine, 2.20; triethylamine, 2.87. The ratio of the ionization constants in water and in methanol for these three cases thus increases as the amine changes from primary to secondary to tertiary.

Summary

The concentration and thermodynamic ionization constants of butylamine, piperidine, triethylamine and of their conjugate acids in methanol at room temperature have been determined by an indicator method.

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[11] Butylamine, pK'_B = 3.39 (Goodhue and Hixon, ref. 10); Piperidine, pK'_B = 2.94 (Wynne-Jones and Salomon, *Trans. Faraday Soc.*, **34**, 1321 (1938)); Triethylamine, pK'_B = 3.13 (Ablard, McKinney and Warner, THIS JOURNAL, **62**, 2181 (1940)).

[COMMUNICATION NO. 980 FROM THE KODAK RESEARCH LABORATORIES]

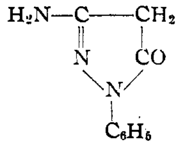
Investigation of Pyrazole Compounds. VI.[1] The Condensation of Some Heterocyclic Hydrazines with Ethyl Cyanoacetate

BY A. WEISSBERGER AND H. D. PORTER

In the first paper of this series[2] it was shown that phenylhydrazine condenses with ethyl cyanoacetate in the presence of sodium ethylate to form 1-phenyl-3-amino-5-pyrazolone, I. This compound readily yields a magenta dye when heated with alcoholic *p*-nitrosodimethylaniline.[3] The isomeric 1-phenyl-3-hydroxy-5-pyrazolone imide, II,[4] produces no dye under the same conditions.[3] If a solution of I is oxidized in the presence of *p*-aminodimethylaniline,[4] or I is subjected to the film-strip test,[5] it forms a bright magenta while with II in either of these oxidation tests only a dull, bluish magenta is obtained.

When 2-pyridylhydrazine was condensed, as above, with ethyl cyanoacetate, a compound resulted which, in its behavior with *p*-nitrosodimethylaniline and in both oxidation tests, resembled II rather than I. The synthesis by means of β-cyanoacetyl-2-pyridylhydrazine, III, in analogy with the synthesis[4] of II, confirmed that the new compound is 1-(2-pyridyl)-3-hydroxy-5-pyrazolone imide, IV. Hence, the condensation of hydrazines with ethyl cyanoacetate does not always yield 3-amino-5-pyrazolones, but can result in 3-hydroxy-5-pyrazolone imides, according to the nature of the hydrazine. This was confirmed by tests with a number of substituted phenylhydrazines and with several heterocyclic hydrazines: *m*-Tolylhydrazine, *m*-chlorophenylhydrazine, *p*-methoxyphenylhydrazine, *p*-sulfamylphenylhydrazine, 3-pyridylhydrazine, and 4-pyridylhydrazine gave the respective 3-amino-5-pyrazolones, while 2-quinolylhydrazine and 2-benzothiazolylhydrazine, like 2-pyridylhydrazine, yielded the respective 3-hydroxy-5-pyrazolone imides. The structures of the pyrazolones were assigned according to the presence or absence of dye formation with *p*-nitrosodimethylaniline and according to the oxidation tests mentioned. Moreover, the two additional 3-hydroxy-5-pyrazolone imides were also synthesized by the cyclization of the respective β-cyanoacetylhydrazines. The resulting 3-hydroxy-5-pyrazolone imides have identical melting points and mixed melting points with the compounds obtained by condensation of the hydrazines with ethyl cyanoacetate.

1-(2-Benzothiazolyl)-3-hydroxy-5-pyrazolone imide is difficult to purify. The identity of the compounds obtained in the condensation of 2-benzothiazolylhydrazine with ethyl cyanoacetate on the one hand, and with cyanoacetazide, on the other hand, was therefore established by comparison of the acetyl derivatives. A diacetyl derivative was prepared from the parent substance with acetic anhydride. Partial deacetylation yielded a mono acetyl compound which forms a dye when subjected to the film-strip test.[5] The mono acetyl derivative is therefore most probably 1-(2-benzothiazolyl)-3-hydroxy-5-pyrazolone acetylimide,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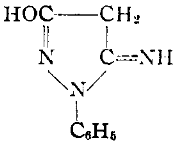
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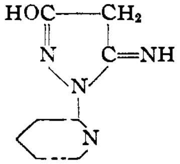
III


IV

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[1] Investigation of Pyrazole Compounds. V, THIS JOURNAL, **65**, 2180 (1943).

[2] Weissberger and Porter, *ibid.*, **64**, 2133 (1942).

[3] Weissberger and Porter, *ibid.*, **65**, 732 (1943).

[4] Weissberger and Porter, *ibid.*, **65**, 52 (1943).

[5] Weissberger and Porter, *ibid.*, **65**, 1495 (1943).