TABLE IV

E.M.F. DATA FOR THE CELLS OF THE TYPE: GLASS/$HClO_4$ (m_1), $Cu(ClO_4)_2$ (m_2), Cu AND THE CORRESPONDING ACTIVITY COEFFICIENT RATIOS

$\frac{m_{H^+}}{m_{Cu^{++}}}$	μ	$(E^0_{glass} - E^0_{Cu^{++}}) - E$	$\frac{\gamma^4_{HClO_4}}{\gamma^3_{Cu(ClO_4)_2}}$
8.122	1.485	0.0490	5.18
	0.986	.0424	4.64
	.558	.0331	4.03
	.279	.0223	3.42
	.1388	.0111	2.91
	.0688	− .0007	2.44
	.0338	− .0140	1.91
6.111	1.498	.0443	4.98
	0.997	.0374	4.49
	.559	.0285	3.94
	.282	.0175	3.37
	.0140	.0064	2.88
	.0695	− .0049	2.39
	.0341	− .0175	1.90
2.007	1.497	.0222	4.71
	1.008	.0160	4.29
	0.572	.0072	3.82
	.285	− .0036	3.30
	.1410	− .0144	2.86
	.0706	− .0259	2.36
	.0344	− .0379	1.89
1.011	1.489	0.0067	4.47
	0.990	.0007	4.20
	.564	− .0081	3.70
	.278	− .0189	3.35
	.1400	− .0296	2.80
	.0700	− .0412	2.27
	.0341	− .0526	1.91
0.779	1.497	.0005	4.32
	1.009	− .0051	4.16
	0.572	− .0139	3.67
	.282	− .0249	3.19
	.1420	− .0358	2.71
	.0705	− .0468	2.26
	.0345	− .0586	1.90
0.397	1.412	− .0177	4.19
	1.010	− .0230	3.90
	0.674	− .0286	3.61
	.342	− .0394	3.22
	.1356	− .0591	2.56
	.0679	− .0649	2.21
	.0263	− .0806	1.69

TABLE V

VARIATION OF ACTIVITY COEFFICIENT RATIO WITH COMPOSITION IN THE SYSTEM $HClO_4$–$Cu(ClO_4)_2$

$\frac{m_{H^+}}{m_{Cu^{++}}}$	μ 0.04	0.08	0.12	0.20	0.40	0.80	1.00	1.20	1.40
8.12	2.04	2.53	2.80	3.17	3.72	4.40	4.66	4.89	5.08
6.11	2.04	2.48	2.76	3.11	3.65	4.28	4.50	4.69	4.88
2.01	2.00	2.45	2.74	3.09	3.56	4.10	4.29	4.46	4.62
1.011	2.00	2.42	2.70	3.03	3.50	4.03	4.20	4.34	4.44
0.779	1.98	2.38	2.62	2.94	3.42	3.95	4.13	4.24	4.30
0.397	1.98	2.30	2.50	2.82	3.31	2.74	3.90	4.03	4.16

where only the activity coefficient ratios are needed.

Attempts to obtain data on two additional systems involving copper salts proved unsuccessful. These systems were nitric acid–cupric nitrate and hydrochloric acid–cupric chloride. In the former case it was found that the spongy copper electrode was attached by even very dilute nitric acid. In the latter instance cupric ion, in the presence of copper, was reduced irreversibly to cuprous ion precipitating from the solution as cuprous chloride.

Acknowledgment.—This research was made possible by a Frederick Gardner Cottrell grant from the Research Corporation.

COLUMBIA, S. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Relative Strengths of Certain Acids in Liquid Ammonia[1]

BY GEORGE W. WATT, DONALD M. SOWARDS AND WILLIAM R. MCBRIDE

RECEIVED JULY 5, 1955

Potentiometric titrations of urea, thiourea and guanidinium acetate and chloride with potassium amide in liquid ammonia at −36° show that the decreasing order of relative acidic strengths of the several acids involved in these systems is: $NH_4^+ > H_2NC(NH)NH_3^+ > H_2NC(S)NH_2 > H_2NC(O)NH_2 > H_2NC(NH)NH_2 > H_2NC(S)NH^- > H_2NC(O)NH^- \geqslant H_2NC(NH)NH^- > NH_2^-$. The monopotassium salts of guanidine, urea and thiourea are soluble in liquid ammonia, while the dipotassium salts are substantially insoluble. The data obtained are discussed with reference to reported properties of these compounds.

Experimental evidence in support of the concept of ammono- and aquoammonocarbonic acids[2,3] consists largely of the displacement of hydrogen from such acids upon reaction with metals in non-aqueous solvents; typical neutralization reactions also have been demonstrated. These reactions have been used in the preparation of salts such as the monosilver and dipotassium salts of guanidine,[4] the mono- and dipotassium salts of urea,[5,6] and the monopotassium salt of thiourea.[7] Despite

---

(1) This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1)-1639 and the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

(2) E. C. Franklin, "The Nitrogen System of Compounds," Reinhold Publ. Corp., New York, N. Y., 1935.

(3) L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953.

(4) E. C. Franklin, THIS JOURNAL, **44**, 490 (1922).

(5) J. S. Blair, *ibid.*, **48**, 97 (1926).

(6) R. A. Jacobson, *ibid.*, **58**, 1984 (1936).

(7) E. A. Werner, *J. Chem. Soc.*, **109**, 1120 (1916).

these rather extensive studies, numerous uncertainties remain. For example, there is no direct evidence for the dipotassium salt of thiourea although it is assumed by analogy with urea. Further, Franklin's statement that guanidine nitrate in liquid ammonia may be considered to be a mixture of nitric acid and guanidine is clearly misleading since the stability of the guanidinium ion in liquid ammonia has been demonstrated by the reversible ammoniation of guanidinium chloride.[8] Also, Werner[9] has expressed doubt that urea can function as a dibasic acid in its reaction with potassium amide in liquid ammonia since urea behaves only as a monobasic acid toward potassium alkoxides in alcohols; this comparison however has been criticized by Blair.[5] In effect, these observations merely reflect the inherent difference in the basic strengths of potassium amide and potassium alkoxides. Finally, it should be recognized that the absolute basicity of a compound varies from solvent to solvent, but the nature of these variations must remain obscure until sufficient data are available for the establishment of relative acidity scales in the different solvents.[10]

Recent work in these laboratories has shown that the neutralization of ammonium ion with amide ion in liquid ammonia may be followed accurately by potentiometric methods.[11] The present paper is concerned with the extension of this procedure to the direct establishment of relative acidities in liquid ammonia. At the same time it was of interest to determine whether the sensitivity of the indicator electrode differs in solutions of compounds of different acidic strengths. The possibly unique applicability of the present method is suggested by the fact that the ultimate formation of a compound of definite composition in a simple displacement reaction does not establish its relative acidity with respect to the displacing agent unless all reactants and products are soluble. Even if these conditions obtain, the possibility of a base-catalyzed reaction which ultimately consumes the base is not eliminated from consideration unless the displacement reaction is reversible under comparable conditions.

Experimental

Materials.—All chemicals employed in this work were strictly anhydrous reagent grade materials. Known weights of redistilled potassium metal contained in glass ampoules[12] were used to prepare potassium amide *in situ* by the iron-catalyzed interaction of potassium and ammonia.

Procedure.—In general, the apparatus and procedures used were the same as those described in detail elsewhere[13]; the mercury-saturated mercury(II) chloride electrode was used as the reference electrode. In a typical experiment, a weighed sample of the acidic compound (*e.g.*, urea) was placed in one buret, a potassium ampoule and an iron wire catalyst were placed in the other buret, the system was evacuated and filled with anhydrous ammonia gas. The potassium ampoule was broken and ammonia was condensed in the burets. An aliquot of the standard acid solution was transferred to the potentiometric titration cell which contained potassium bromide that was used both as a supporting electrolyte and to minimize the solubility of the dipotassium salts formed in the ensuing neutralization reactions; the acid solution was then titrated with standard potassium amide solution. Solution concentrations ranged from 0.04 to 0.10 *N*, the solutions were stirred with anhydrous oxygen-free nitrogen, the pressure was approximately 5 mm. above atmospheric pressure, and the temperature was $-36 \pm 1°$.

Typical results obtained in the titration of the dibasic acids urea and thiourea, and the tribasic acid guanidinium acetate are given in Fig. 1. Substitution of guanidinium chloride for guanidinium acetate gave essentially the same results despite the relative insolubility of potassium chloride. The monopotassium salts of urea, thiourea and guanidine were soluble under the conditions of concentration used; the dipotassium salts however separated as relatively insoluble white voluminous solids. In order to determine the relative acidic strengths of these acids, mixtures of two acids in a mole ratio of 1:2 were titrated with potassium amide as described above. Typical results from these titrations are shown in Fig. 2, from which it is seen that the individual stoichiometric end-points and the internal agreement between end-points is entirely satisfactory.

Two minor difficulties concerned with electrode behavior were encountered during the course of these titrations. It was found that solutions of thiourea, and possibly guanidinium salts, react with the mercury(II) chloride, thus altering measurably the working potential of this reference electrode. Accordingly, the present data cannot be used for the estimation of thermodynamic quantities. Also, the presence of the insoluble dipotassium salts affects the potential of the platinum indicator electrode to an extent that depends upon whether or not the solid is in contact with this electrode. Neither of these complications however appears to influence either the reproducibility of the end-points or the reliability of the interpretation of these data.

Discussion

The data of Fig. 1 provide evidence for the occurrence of the reactions

$$H_2NC(S)NH_2 + KNH_2 \longrightarrow K[H_2NC(S)NH] + NH_3 \quad (1)$$

$$H_2NC(O)NH_2 + KNH_2 \longrightarrow K[H_2NC(O)NH] + NH_3 \quad (2)$$

$$[H_2NC(NH)NH_3]CO_2CH_3 + KNH_2 \longrightarrow H_2NC(NH)NH_2 + CH_3CO_2K + NH_3 \quad (3)$$

$$H_2NC(NH)NH_2 + KNH_2 \longrightarrow K[H_2NC(NH)NH] + NH_3 \quad (4)$$

$$K[H_2NC(NH)NH] + KNH_2 \longrightarrow K_2[HNC(NH)NH] + NH_3 \quad (5)$$

all of which are typical of neutralization reactions in ammonia. These data also show the relative strengths of the three acidic species involving guanidine, *i.e.*, the acids shown on the left in equations 3, 4 and 5.

Figure 2 gives supporting evidence for certain of these reactions and also for the occurrence of the reaction

$$K[H_2NC(S)NH] + KNH_2 \longrightarrow K_2[NHC(S)NH] + NH_3 \quad (6)$$

These results also show the orders of relative strengths among the pairs of acids present at various times during the titrations, assuming of course that the strongest acid present reacts preferentially with the base, potassium amide. Thus, on the basis of Fig. 1 together with a knowledge of the solubilities of the salts formed, the lower curve for the titration of a mixture containing thiourea and urea

---

(8) G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 2751 (1955).

(9) E. A. Werner, "The Chemistry of Urea," Longmans, Green and Co., London, 1923, p. 112.

(10) B. Gutbezahl and E. Grunwald. THIS JOURNAL, **75**, 565 (1953).

(11) G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 46 (1955).

(12) G. W. Watt and D. M. Sowards, THIS JOURNAL, **76**, 4742 (1954).

(13) G. W. Watt and D. M. Sowards, *J. Electrochem. Soc.*, **102**, 545 (1955).

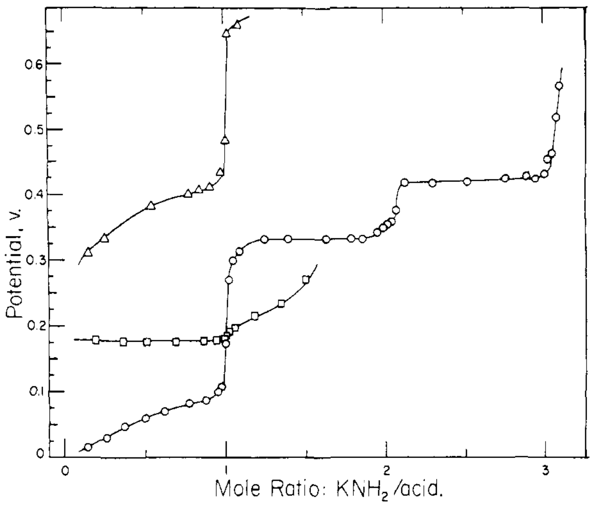

Fig. 1.—Potentiometric titration of urea, thiourea and guanidinium acetate with potassium amide in liquid ammonia: □, urea; △, thiourea; ○, guanidinium acetate.

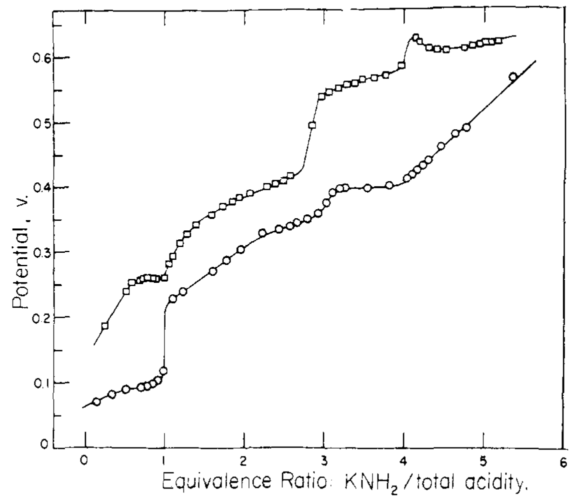

Fig. 2.—Potentiometric titration of mixtures of urea and thiourea and of thiourea and guanidinium acetate with potassium amide in liquid ammonia: ○, urea and thiourea, 2:1; □, thiourea and guanidinium acetate, 2:1.

in a mole ratio of 1:2 is interpreted as follows. The equivalence ratio ranges of 0 to 1, 1 to 3, and 3 to 4 correspond to the occurrence of reactions 1, 2 and 6, respectively. The range from 4 to the end of the curve corresponds to the reaction

$$K[H_2NC(O)NH] + KNH_2 \longrightarrow K_2[HNC(O)NH] + NH_3 \quad (7)$$

The other curve in Fig. 2 may be interpreted similarly; thus one arrives at the following decreasing order of strengths of the acidic species that are involved in these liquid ammonia solutions

$$NH_4^+ > H_2NC(NH)NH_3^+ > H_2NC(S)NH_2 > H_2NC(O)NH_2 > H_2NC(NH)NH_2 > H_2NC(S)NH^- > H_2NC(O)NH^- \geqslant H_2NC(NH)NH^- > NH_2^-$$

Although ammonia is most often considered as an acid-leveling solvent[3] because the strongest acid capable of existence in solution is the ammonium ion, the results given above show further that ammonia acts as an acid-differentiating solvent for weak proton-donor acids. Thus, all acids in this solvent must have strengths that lie within the range of acidities from that of NH_4^+ to that of NH_2^-.

There is still other experimental evidence in support of the order of acidic strengths given above. Thiourea, urea and guanidine are bases in aqueous solution and it is seen from Table I that their ionization constants, K_b, may be correlated with the dissociation pressures of the corresponding 1-ammoniates.[8,14]

In the gas–solid reaction between ammonia and thiourea, the latter must behave as a Lewis acid with respect to ammonia, and if the dissociation pressure of the resulting ammoniate is indicative of the bond strength, it follows that urea and guanidine are both weaker Lewis acids than thiourea. With respect to the invariant systems involving the saturated solutions, it is possible to determine the relative acidities of thiourea and urea but not of urea and guanidine. Since the extent of ammoniation should increase in a regular fashion according to the relative strengths of the acids, thiourea might be expected to form ammoniates higher than the 1-ammoniate. A 3-ammoniate of thiourea has indeed been detected[15] but there is no evidence for the formation of higher ammoniates of either urea or guanidine.[14] Thus for these three compounds the acidity in liquid ammonia, the basicity in water, and the stability of the ammoniates are all determined by the same factor, *i.e.*, proton affinity.

TABLE I

IONIZATION CONSTANTS OF THIOUREA, UREA AND GUANIDINE IN AQUEOUS SOLUTION AND THE DISSOCIATION PRESSURES OF THEIR 1-AMMONIATES

		Dissociation pressure, mm.; invariant systems at −35°	
	K_b, 25°	1-Ammoniate[a]	Satd. soln.[b]
Thiourea	1.1×10^{-15}	33	495
Urea	1.5×10^{-14}	104	~703
Guanidine	$\sim 1 \times 10^{-2}$	220	~703

[a] Phases present: gaseous ammonia, the deammoniated compound and the 1-ammoniate. [b] Phases present: gaseous ammonia, the 1-ammoniate and the saturated solution of the 1-ammoniate.

Collectively, the experimental evidence cited above shows that the relative order of the contribution of :S, :O, and :NH to the acidic strength is not changed in the sequence of reactions

$$[HNC(X)NH]^- + H^+ \longrightarrow [H_2NC(X)NH]^-$$
$$[H_2NC(X)NH]^- + H^+ \longrightarrow H_2NC(X)NH_2$$
$$H_2NC(X)NH_2 + H^+ \longrightarrow [H_2NC(X)NH_3]^+$$
$$H_2NC(X)NH_2 + NH_3 \longrightarrow [H_2NC(X)NH_2]\cdot NH_3$$

where X = :S, :O, or :NH, and H^+ represents the solvated proton.

Finally, it should be pointed out that this work suggests the possibility of using these compounds and their salts for the preparation of buffered solutions in liquid ammonia.

AUSTIN, TEXAS

---

(14) G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 5795 (1955).

(15) E. Janecke and A. Hoffmann, *Z. Elektrochem.*, **38**, 880 (1932).