potassium iodide in a hydrogen atmosphere, experiments were performed using samples dried simply at 200–225°. The normalities obtained with the unfused salt were 0.02 to 0.03% higher than with the fused salt, indicating the retention of a very small amount of occluded water.

3. Although sodium oxalate and oxalic acid are classical primary standards, they are not suitable for the highly exact standardization of potassium permanganate solutions because of side reactions. Theoretical results can be found only by a compensation of errors. In agreement with Fowler and Bright[8] we found in the present work that McBride's procedure gives high normalities (average +0.20%), the precision of the titration being not greater than ±0.1% The procedure recommended by Kolthoff[7] gives slightly better results, although the average error was still +0.13%. The best results were obtained by Fowler and Bright's procedure, although even in this case the average error amounted to +0.07% as referred to potassium iodide. Therefore, potassium iodide and arsenious oxide fulfill the rigid requirements of primary standard substances better than sodium oxalate.

Acknowledgment.—We express our appreciation to the Graduate School of the University of Minnesota for financial aid which enabled us to do this work.

Summary

1. Potassium iodide and arsenious oxide are more suitable for the exact standardization of potassium permanganate than sodium oxalate.

2. The results obtained by the potentiometric titration of pure potassium iodide and of Bureau of Standards arsenious oxide with potassium permanganate agreed within 0.03%.

3. Potassium permanganate may be standardized against potassium iodide by Andrews' method or by Lang's method under the specified conditions. The results were accurate within 0.05%.

4. The results obtained with potassium iodide dried at 200–225° were 0.025% higher than with fused samples of the salt.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 10, 1936

[CONTRIBUTION FROM THE LABORATORY OF LIQUEFIED GASES OF THE KARPOV INSTITUTE FOR PHYSICAL CHEMISTRY]

A Study of Acid Catalysis in Liquid Ammonia

BY A. I. SHATENSHTEIN

Brönsted's work cleared up the concept of the acid–base equilibrium in any solvent. The solvent participates together with the dissolved substance in a double buffer equilibrium

$$\text{acid}_1 + \text{base}_2 \rightleftharpoons \text{acid}_2 + \text{base}_1 \qquad (1)$$

This unified point of view enables one to correlate phenomena observed in different solvents, and in particular the catalysis of solvolysis reactions in aqueous and ammoniacal solutions.

From experimental results obtained in the catalysis of sugar inversion by concentrated aqueous solutions of acids it is evident[1] that the specific catalytic activity (ratio of the reaction velocity constant to the equivalent concentration of the acid) rises (as the concentration of the acid increases) in the case of perchloric, hydrobromic, hydrochloric and nitric acids (acids given in descending order of specific catalytic activity). This ratio remains constant in a solution of trichloroacetic acid and in solutions of the weaker acids the lower the dissociation constant of the acid the lower it falls.

The sequence of acids shown corresponds to the increasing firmness with which the proton is held in the molecule of acid and at the same time corresponds (for the so-called "strong" acids) to the increase of the interionic forces in their ionized solutions.

The rise in the specific catalytic activity can be attributed[2] to the primary salt effect, which may be more correctly described as the primary autosalt effect. This is really the influence of the field of forces of the ions surrounding the solvatized protons $(H_3O\cdot nH_2O)^+$ and the reacting molecules. The increase in the concentration of the ionized acid corresponds to an increase in the strength of the field and the decrease in the degree of solvatization of the ions.

Assuming equally complete ionization in concentrated aqueous solutions of all "strong" acids, one might expect greater catalytic activity of

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[1] A. Hantzsch and A. Weisberg, *Z. physik. Chem.*, **125**, 251 (1927).

[2] J. Brönsted and Bell, THIS JOURNAL, **53**, 2478 (1931).

those acids in which the interionic forces are greatest. Actually, however, the opposite phenomenon is observed.

The contradiction may be solved by assuming that the reaction of solvolysis (of the sugar inversion type) is catalyzed, in the main, by lyonium[3] ions and that in concentrated aqueous solutions of "strong" acids one has a secondary auto-salt effect, that is to say, an unequally complete displacement of the equilibrium (1) in the direction of forming undissociated molecules of acid. This is confirmed by Raman spectra.[4]

The addition to the acid solution of a neutral salt with a common anion has the same effect on the reaction velocity as raising the concentration of the acid.[5] This confirms the applicability of the term auto-salt effect to the phenomena observed when the concentration of the acid is raised.

Thus one may take it that the change in the specific catalytic activity of aqueous solutions of acids as their concentration increases is the total result of primary and secondary auto-salt effects and depends on which of these predominates.

Assuming this view to be correct and taking into account the properties of ammonia, which is a solvent with a considerably greater affinity for the proton than water and a much lower dielectric constant, one may make a prediction with regard to the acid catalysis of the ammonolysis of organic compounds (ethers, lactones, etc.) in liquid ammonia.

Equilibrium (1) is displaced much farther to the right in solutions of acids in liquid ammonia than in water. The effect of interionic forces is much stronger in liquid ammonia than in water.

From this the following conclusions can be drawn: Reactions of ammonolysis in liquid ammonia should be catalyzed by phenols, amides and imides of acids,[6] and carbohydrates. In concentrated solutions of these acids both a primary and a secondary auto-salt effect occur. The catalytic activity of dilute solutions of ammonium salts of "strong" inorganic and "weak" organic acids should be the same and should be proportional to the analytic concentration of the solvatized protons $(NH_4 \cdot nNH_3)^+$.

When the concentration of solutions of "strong" acids is increased the secondary auto-salt effect is absent.[7] Assuming that the catalytic activity of solvatized protons increases as the field of forces of the anions becomes stronger, one may expect that a series of acids, placed in ascending order of specific catalytic activity, will be antibatic to a series of acids placed in ascending order to electrical conductivity, activity and osmotic coefficients.

The aim of the present work was to test these conclusions.

Experimental Results

The velocity of the reactions was measured by the change in the rotation of the plane of polarization of a solution in liquid ammonia. For this purpose a method was worked out for polarimetric measurements in liquefied gases at room temperature.[8] The reaction velocity constants were calculated according to the equation for a reaction of the first order.

In Table IV time is expressed in hours and in the other tables in minutes. The temperature in all cases was 20 ± 0.2°.

I. Kinetics of Ammonolysis of Santonine.—As Abkin and Medvedev[9] have shown the ammonolysis of santonine in liquid ammonia proceeds quantitatively with the formation of the amide of santoninic acid.

The reaction takes place autocatalytically. The initial value of the reaction velocity constant at 20° is about 0.0004.

A. Catalysis by Ammonium Salts.[10]—In Table I the average values of reaction velocity constants of the ammonolysis of santonine in the presence of ammonium salts are given.

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[3] Undissociated molecules of an acid can only play a minor part in the catalysis of reactions of solvolysis: the more easily they yield up a proton the greater is the probability of "lyonium" ions being formed.

[4] J. Hibben, *Chem., Rev.*, **13**, 345 (1933); R. Fonteyne, *Nature*, **138**, 886 (1936).

[5] Spohr, *J. prakt. Chem.*, **32**, 32 (1885).

[6] That solutions of these substances in liquid ammonia act as acids has been shown in numerous researches by Franklin (see E. C. Franklin, "Nitrogen System of Compounds," A. C. S. Monograph Series, 1935).

[7] M. Wolkenstein (*Acta Physicochim., U. R. S. S.*, **5**, 627 (1936)) has actually shown that in the Raman spectra of concentrated solutions of NH_4NO_3 and NH_4CNS in liquid NH_3 no frequencies are observed which could be ascribed to undissociated molecules. Of course when the concentration is increased a change in the degree of solvatization of ions, including $(NH_4 \cdot nNH_3)^+$ is possible. Between ions in ammonia solutions of organic carboxyl acids, beside electrostatic forces there are also forces of a chemical nature.[14] These would also appear to be present in concentrated solutions of inorganic acids, and this should have an influence on their catalytic activity. Owing to the lack of material this question is not discussed in the present paper.

[8] A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **3**, 53 (1935).

[9] A. Abkin and S. Medvedev, *J. Gen. Chem., U. S. S. R.* (in Russian), **4**, 1402 (1934).

[10] For details see A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **3**, 37 (1936).

TABLE I

REACTION VELOCITY CONSTANT OF AMMONOLYSIS OF SANTONINE IN THE PRESENCE OF AMMONIUM SALTS[11]

N	$NH_4O_2CCH_3$	NH_4Cl	NH_4Br	NH_4NO_3	NH_4I
0.01	0.0043	0.0055	0.0054	0.0053	0.0054
.03	...	.0154	.0150	.0118	.0157
.05	.0197	.0242	.0248	.0221	.0236
.10	.0419	.0492	.0466	.0433	.0412

N	NH_4ClO_4	NH_4O_2CH	NH_4O_2-CC_6H_5	NH_4O_2-CCH_2CN	NH_4CNS
0.10	0.0386	0.0410	0.0404	0.0428	0.0408

Table II shows the effect of adding neutral salts.

TABLE II

ACTION OF NEUTRAL SALTS

	Without salt	NaI (1 N)	$NaNO_3$ (1 N)	NaBr (1 N)
NH_4NO_3 (0.05 N)	0.0221	0.0220	0.0233	0.0291
NH_4Br (0.05 N)	.0248	.0235	.0265	.0300

In all cases the concentration of santonine was about 2.75 g. per 100 cc. of the solution. The reproducibility of the experiments was within 3 to 5%. As an example the following are the values for the velocity constant in one of the experiments: ($K \times 10^4$): 108, 118, 116, 115, 114, 115, 112, 114, 116, 115, 116, 114, 110, 107; average 0.0114.

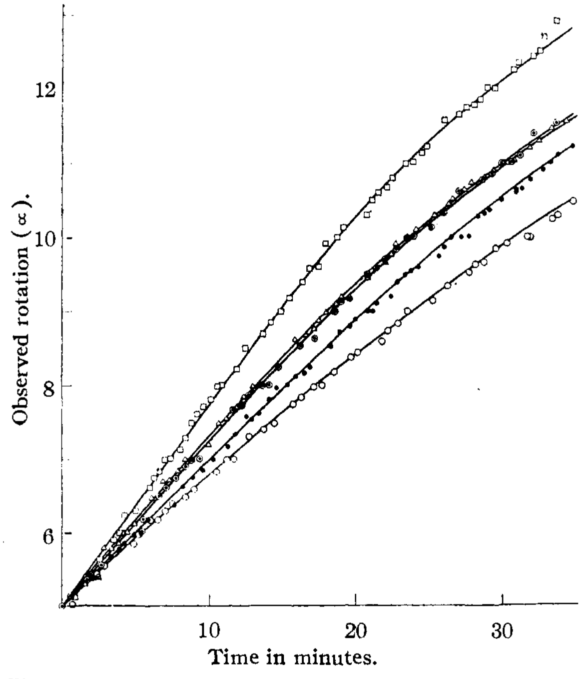

Fig. 1.—□, NH_4Cl; △, NH_4Br; ◉, NH_4NO_3; ●, NH_4I; ○, NH_4ClO_4.

B. Catalysis by Amides of Acids, etc.—Table III shows results of provisional measurements of the reaction velocity of the ammonolysis of santonine in the presence of amides of acids, phenol, etc.

TABLE III

REACTION VELOCITY CONSTANT OF AMMONOLYSIS OF SANTONINE IN THE PRESENCE OF AMIDES OF ACIDS, ETC.

Contents of table: 1, name of catalyst; 2, concentration of catalyst (moles); 3, reaction velocity constant (average); 4, calculated reaction velocity constant for a concentration of catalyst of 1 N (one NH_2 or OH group).

1	2	3	4
Glucose	0.49	0.0006	
Acetamide	.98	.0021	0.0021
Urea	.98	.0067	.0034
Carbazole	.44	.0024	.0055
Benzamide	.99	.0065	.0065
Cyanacetamide	.48	.0051	.0106
Phenol	.20	.0086	.0424
Formamide	1.82	.101	.0621

II. Kinetics of the Ammonolysis of Desmotroposantonine in the Presence of Ammonium Salts.[12]—It may be thought that by analogy with the ammonolysis of santonine an amide of the desmotroposantoninic acid is formed as an end-product.

Table IV gives the average values of the reaction velocity constants in the presence of 1.5-normal solutions of ammonium salts (concentration of desmotroposantonine 0.75 g. per 100 cc. of solution).

TABLE IV

REACTION VELOCITY CONSTANTS OF THE AMMONOLYSIS OF DESMOTROPOSANTONINE

N	NH_4Cl	NH_4Br	NH_4I
1.5	0.024	0.015	0.010

The reproducibility of the constants was within 5 to 10%.

III. Kinetics of the Ammonolysis of Ethyl Tartrate in the Presence of Ammonium Salts.—The reaction took place with the formation of the diamide of tartaric acid. Figure 1 gives an idea of the velocity of the reaction of the ester in the presence of a number of ammonium salts (1.02 N). Concentration of ester 15.2 g. to 100 cc. of solution.

Discussion of Results

The experimental material submitted confirms the propositions given above regarding acid catalysis in liquid ammonia.

From Tables I–IV and Fig. 1 it follows that as concentration increases the catalytic activity of

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(11) The last four results are provisional.

(12) For details see A. Schattenstein, *Acta Physicochim., U. R. S. S.*, **5**, 841 (1936).

ammonium salts of "strong" acids varies with the anion as follows: $ClO_4^- < I^- < NO_3^- < Br^- < Cl^-$.

In the works of Schattenstein and Uskova,[13] Gurjanova and Pleskov[14] it has been shown that the osmotic coefficients and coefficients of electrical conductivity of solutions of ammonium salts in liquid NH_3 follow in the order: $ClO_4^- > I^- > NO_3^- > Br^- > Cl^-$.

Similar data with regard to solutions of halogen salts and nitrates of alkali metals have been published in the works of Linhard[15] and Kraus.[16]

The order of catalytic activity of the amides of carboxyl acids in liquid ammonia corresponds to that of the acids themselves in water ($CH_3COOH < C_6H_5COOH < HCOOH$). There are no quite reliable data for the electrical conductivity of the amides of acids and phenols especially at great dilutions, on a basis of which one can calculate the coefficients of electrical conductivity of these solutions and corresponding dissociation constants. However, the qualitative comparison of our data with the results of Franklin and Kraus' work[17] on the whole confirm the proposition stated above.

Thus to sum up it may be asserted that the experimental material which we have hitherto been able to collect, is in good agreement with the views expressed in the present paper. This makes them quite plausible. However, further research is necessary to establish them on a firmer basis and pass from purely qualitative reasoning to stricter conclusions. Work is still in progress.

Acknowledgment.—The author wishes to thank Prof. A. M. Monossohn for his kind attention and interest in the present work.

Summary

1. The suggestion is made that the change in the specific catalytic activity of acids (including "strong" acids) as the concentration of their aqueous solutions rises is the total result of the primary and secondary auto-salt effects.

2. The conclusions are drawn as regards the acid catalysis of the ammonolysis reaction in liquid ammonia which are tested experimentally in the case of the ammonolysis of santonine, desmotroposantonine and ethyl tartrate.

3. Ammonolysis reactions in liquid ammonia are catalyzed by ammonium salts, amides of acids, phenols and carbohydrates.

4. The differences in catalytic activity of ammonium salts, both of "strong" and "weak" acids are leveled out. In dilute solutions the velocity constant is proportional to the concentration of the solvatized protons. With increase in concentration in solutions of ammonium salts of "strong" acids the antibatic nature of the series of catalytic activity and the series of electrical conductivity, activity and osmotic coefficients is observed.

5. The relationships usual in aqueous solutions of acids are observed in ammonia solutions of acids in which the proton is firmly attached (*e. g.*, the amides of acids).

MOSCOW, U. S. S. R. RECEIVED AUGUST 10, 1936

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[13] A. Schattenstein and L. Uskova, *Acta Physicochim., U. R. S. S.*, **2**, 37 (1935).

[14] E. Gurjanova and V. Pleskov, *ibid.*, **5**, 509 (1936).

[15] M. Linhard, *Z. physik. Chem.*, **175**, 438 (1936).

[16] C. A. Kraus, *J. Chem. Ed.*, **12**, 567 (1935).

[17] E. Franklin and C. A. Kraus, THIS JOURNAL, **27**, 191 (1905).