TABLE V

ACID STRENGTH OF SINTERED SILICA–ALUMINA

Catalyst history[a]	H_0
Unsintered	< -8.2
Heated to 880° *in vacuo*	< -8.2
Steamed 120 hr. at 575°	-5.6 to -8.2
Used at refinery	< -8.2

[a] Calcined at 550° immediately before carrying out indicator tests.

The resulting data show that sintering the above samples at high temperatures *in vacuo*[18] or by use in the refinery has no measurable effect on the acid strength of silica–alumina catalyst. Steaming, however, decreases its acid strength.

Neutralization of Surface Acidity.—As was indicated by the data listed in Table III, the acidity of clays and cracking catalysts is not completely neutralized by titrating such solids with aqueous sodium hydroxide. When the titrated solid is filtered off and dried, the product is still acid though the strength is reduced in most cases. However, any acid surface can be neutralized to all Hammett indicators by addition of ammonia or an amine either in the vapor state or in an inert solvent such as benzene or isoöctane.

As might be anticipated, the adsorption of most polar molecules (*e.g.*, water, alcohols, ketones, ethers and even organic acids) lowers the strength of acid surfaces, the extent of the lowering depending on the basicity and concentration of the molecule being adsorbed.

Conclusions.—The results obtained in this investigation show that the use of Hammett indicators in measuring acid strengths of solid surfaces can furnish useful information not readily obtainable by other means. Because the technique is so simple, it is particularly suitable for screening catalysts prepared in the laboratory, and for making rapid surveys of solids where surface acidity is of possible interest.

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(18) Samples furnished by Dr. E. E. Roper.

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

The Ammoniation, Ammonolysis and Hydrolysis of Aluminum(III) Iodide[1]

BY GEORGE W. WATT AND JUERGEN H. BRAUN

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Aluminum(III) iodide and its 6-ammoniate have been shown to be unusually susceptible to hydrolysis, but under appropriate conditions, liquid ammonia solutions of the iodide that are free of hydrolysis products may be prepared. The solid phase that separates at −68° is the 20-ammoniate; at −33.5°, the 6-ammoniate. The latter is not ammonolyzed even at 110°. The bearing of these and other results upon the question of the existence of lower oxidation states of aluminum in liquid ammonia solutions is discussed.

Recent publications from this Laboratory[2] and elsewhere[3–6] have been concerned with somewhat controversial evidence for the existence of lower oxidation states of aluminum in liquid ammonia. Data obtained from potentiometric titrations of aluminum(III) iodide with potassium in liquid ammonia[2] and interpreted as evidence for the transitory existence of lower oxidation states of aluminum have alternatively been interpreted[5,6] as attributable to the reduction of ammonium ion resulting from the ammonolysis of aluminum(III) iodide. The results given below suggest that this latter interpretation is highly improbable.

Despite rather extensive studies on systems comprising aluminum(III) iodide and ammonia under a variety of conditions,[7–10] several features of the chemistry of this salt in liquid ammonia remain obscure. Accordingly, we have studied the ammoniation, ammonolysis, and hydrolysis of this salt, and the significance of these reactions in relation to the question of evidence for the existence of lower oxidation states of aluminum in ammonia.

Experimental

Materials.—Aluminum(III) iodide was prepared by a modification of a method described previously[11]; samples prepared with a view to total exclusion of water were placed and stored in fragile glass ampoules by an adaptation of the method[12] previously described for the manipulation of samples of alkali metals. Unless otherwise indicated, these sealed ampoules were not opened except in the presence of ammonia or nitrogen under anhydrous oxygen-free conditions.

With the exception of experiments designed to evaluate the effect of the presence of water, the above and all other materials employed were strictly anhydrous reagent grade chemicals.

Ammoniation of Aluminum(III) Iodide.—After extensive experiments designed to provide conditions under which the ammoniation of this salt could be accomplished without the

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(1) This work was supported in part by the Atomic Energy Commission, Contract AT-(40-1-)-1639.

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occurrence of either hydrolysis or ammonolysis, the following procedure was found to meet these objectives. A sealed ampoule containing 1.0 g. of aluminum(III) iodide was placed in a 1.8 cm. o.d. Pyrex tube bearing a fritted glass filter at the mid-point. The tube was evacuated, dried and cooled to and maintained at −68°. Anhydrous ammonia gas was condensed (20 ml.), the tube was sealed, the ampoule was broken, and the iodide dissolved slowly over a period of 1 hr. to provide a perfectly *clear solution*. Upon agitation of this solution, elongated crystals of $AlI_3 \cdot 20NH_3$[13] separated. These crystals exhibit a high ammonia vapor pressure and melt in an ammonia atmosphere at −26°.

Because of the need for a method (in addition to melting point) for the *in situ* characterization of $AlI_3 \cdot 20NH_3$, a procedure for the measurement of the characteristic extinction angle[14,15] of these crystals in the presence of liquid ammonia was devised. Two polaroid disks 5 cm. in diameter were mounted 3.5 cm. apart in crossed position. A cross-hair indicated the planes of vibration of the polarized light for the polarizer and analyzer. This mounting was placed in a box and arranged so that the mounting could be turned in a suitable frame. The sealed tube containing $AlI_3 \cdot 20NH_3$ crystals was inserted between the disks and these were turned until the cross-hair was parallel to the long axis of the crystal selected. The position of the cross-hair was marked on the frame and the extinction angle was determined graphically following removal of the tube containing the crystals. Several measurements were made on different crystals and the maximum extinction angle was taken as that characteristic of this particular ammoniate; the value found was 71 ± 5°.[16]

When solutions prepared as described above were warmed to −33.5°, the solvent was evaporated, and the tube evacuated at 10^{-3} mm. at 25°, white crystals of $AlI_3 \cdot 6NH_3$ remained. *Anal.* Calcd. for $AlI_3 \cdot 6NH_3$: Al, 5.29; I, 74.7; N, 16.5. Found: Al, 5.33; I, 74.3; N, 16.7. Crystals (1 to 3 mm. in diameter) having the same composition but prepared by the interaction of aluminum amalgam and ammonium iodide in liquid ammonia (see below) were found to consist of hexagonal bipyramids $\{10\bar{1}0\}$ with basal pinacoid {0001}. When viewed perpendicular to the (0001) plane, these crystals appeared to be isotropic; parallel to this plane they showed maximum birefringence.

Again with a view to the *in situ* preparation of liquid ammonia solutions of ammoniated aluminum(III) iodide under conditions that preclude the possibility of either hydrolysis or ammonolysis, 28 mg. of clean aluminum wire in contact with a platinum wire was sealed in a tube containing 1.0 g. of ammonium iodide in 20 ml. of liquid ammonia. There was no evidence of reaction after 1 hr. at −33.5°, 1 hr. at 0°, 12 hr. at 25°, or 27 hr. at 115°. Analysis of the ammonia solution showed that only traces of Al^{3+} were present. In similar experiments, 86.6 mg. of clean aluminum wire, 3 ml. of mercury and 0.30 g. of ammonium iodide were sealed in a Pyrex tube of 11 cm. o.d. and 0.2 cm. wall thickness with a fine porosity fritted glass disc at the mid-point. After drying this tube and its contents for 12 hr. at 10^{-3} mm., anhydrous ammonia was condensed in the tube at −70° to provide 3.0 ml. of solution. Hydrogen evolution was first observed at −40° and continued for 10 days at 25°. The solution was filtered and cooled to −70°, whereupon crystals of $AlI_3 \cdot 20NH_3$ having an extinction angle of 70 ± 5 separated. When the clear solution was warmed to room temperature, crystals of $AlI_3 \cdot 6NH_3$ separated.

By determining the volumes of ammonia required to dissolve known weights of aluminum(III) iodide 6-ammoniate, the solubility of aluminum(III) iodide in liquid ammonia was estimated. With $AlI_3 \cdot 20NH_3$ as the solid phase in equilibrium with the saturated solution at −42°, the solubility was found to be 2.4 g. AlI_3/100 ml. of solution. With $AlI_3.6NH_3$ the solid phase at 25°, the solubility was 10 g. AlI_3/100 ml. of solution.

The Ammonolysis of Aluminum(III) Iodide.—A solution of 1.0 g. of aluminum(III) iodide in 20 ml. of liquid ammonia was prepared as described above and sufficient time at −68° was allowed for separation of crystals of $AlI_3 \cdot 20NH_3$, the estimation of the volume occupied by these crystals, the measurement of the extinction angle of 70 ± 5°, and the melting point of −26°. The sealed tube was then heated in an autoclave for 72 hr. at 110°. The tube was removed from the autoclave and cooled to −68°, whereupon crystals of $AlI_3 \cdot 20NH_3$ separated in a quantity indistinguishable from that present before elevation of the temperature. The measured extinction angle of these crystals was 69 ± 5° and they melted at −26°. Thus, *there was no evidence of ammonolysis despite a 178° elevation in temperature for 72 hr.*

Thermal Decomposition of Aluminum(III) Iodide 6-Ammoniate.—Aluminum(III) iodide 6-ammoniate (0.8913 g., 1.75 millimoles) was heated to 340° at a pressure of 10^{-2} mm. in a closed system designed to permit the collection and analysis of gaseous products. Gas evolution was first detectable at 220°, became rapid at 250°, and was essentially complete at 300°; a total of 1.8 millimoles of ammonia gas was collected. The white solid sublimed coincident with gas evolution; the sublimate was collected and analyzed. *Anal.* Calcd. for $AlI_3 \cdot 5NH_3$: Al, 5.5; N, 14.2. Found: Al, 5.5; N, 13.8. This product dissolved in liquid ammonia at −33.5° and upon cooling the resulting solution to −68°, characteristic crystals of $AlI_3 \cdot 20NH_3$ separated.

Hydrolysis of Aluminum(III) Iodide and Aluminum(III) Iodide 6-Ammoniate.—In preliminary qualitative experiments, both aluminum(III) iodide and its 6-ammoniate were deliberately exposed to the atmosphere for varying periods of the order of 5–10 sec. before dissolution in liquid ammonia under otherwise anhydrous conditions. In both cases, the resulting ammonia solutions were turbid to an extent dependent upon the duration of prior exposure of the solids to the atmosphere. After dissolution, however, the degree of turbidity was uninfluenced by either time or temperature variations over the range −68 to 30°. The quantities of solid present were too small to permit isolation and in most cases did not exceed a few milligrams. In other experiments, pure aluminum(III) iodide 6-ammoniate was given only momentary exposure to the atmosphere during efforts to get an X-ray diffraction pattern for the 6-ammoniate. In all such cases, the presence of ammonium iodide was established by comparison of the patterns obtained with data given in the A.S.T.M. Index of X-ray diffraction patterns. The hydrolysis of the 6-ammoniate was accelerated by heating in air; complete hydrolysis yielded either α- or γ-Al_2O_3[17] depending upon the final ignition temperature.

In other experiments, of which the following are typical, the weight changes that accompany the hydrolysis of aluminum(III) iodide 6-ammoniate were measured. When 187.2 mg. of the ammoniate was exposed to the normal laboratory atmosphere for 12 hr. at 25°, the final weight was 191.2 mg. Similarly, when 187.2 mg. was exposed to air saturated with water vapor at 25° for 6 hr., the final weight was 196.5 mg. Finally, when 229.5 mg. of $AlI_3 \cdot 6NH_3$ (16.48% nitrogen) and dilute sulfuric acid (in separate containers) were equilibrated for 12 days, the resulting solid contained 8.03% nitrogen and the sulfuric acid solution contained 53.5% of the nitrogen introduced initially as the 6-ammoniate.

Discussion

These experiments are mainly concerned with whether aluminum(III) iodide ammonolyzes in liquid ammonia to form ammonium ion and insoluble[6,18] ammonolysis products such as $Al(NH_2)I_2$ or $Al(NH_2)_3$. The results described above show that, under conditions that provide for both total exclusion of water and dissipation of heat of ammoniation, perfectly clear stable solutions of aluminum(III) iodide may be prepared, and *insoluble*

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[13] The composition of this solid phase was first reported by Franklin[7] and subsequently confirmed by Klemm and Tanke (W. Klemm and E. Tanke, *Z. anorg. allgem. Chem.*, **200**, 343 (1931)).

[14] A. F. Rogers and P. F. Kerr, "Optical Mineralogy," McGraw-Hill Book Co., Inc., New York, N. Y., 1942, p. 79.

[15] C. W. Bunn, "Chemical Crystallography," Oxford University Press, Glasgow, 1946, p. 99.

[16] Although such measurements are conventionally made using a polarization microscope, this technique is impractical for crystals that are stable only in an ammonia environment at temperatures below −26°.

[17] Also identified by means of X-ray diffraction patterns.

[18] F. W. Bergstrom, *J. Phys. Chem.*, **32**, 433 (1928).

ammonolysis products are not observed even when these solutions are heated from -68 to 110° and held at the latter temperature for 72 hr. It seems highly improbable that there exists at $-68°$ a solvolytic equilibrium that provides any detectable concentration of ammonium ion and that is temperature independent.

The properties of the ammoniates of aluminum (III) iodide also argue against the occurrence of ammonolysis. The experiments described above demonstrate the conversions

$$AlI_3\cdot 20NH_3 \rightleftarrows AlI_3\cdot 6NH_3 \rightleftarrows AlI_3\cdot 5NH_3$$

The 6-ammoniate is stable in ammonia solution up to at least 110° and is formed reversibly from the 20-ammoniate; the 5-ammoniate is stable in gaseous ammonia up to 220° and reverts to the 20-ammoniate when dissolved in liquid ammonia.

In the light of the results described above, the turbidity commonly observed when aluminum(III) iodide is dissolved in ammonia[7,19,20] is most probably attributable to the presence of hydrated aluminum(III) oxide (or possibly its precursors, *i.e.*, *aquo*-basic iodides) resulting from the unusual susceptibility of the iodide to hydrolysis. The earlier conclusion[6] that these solids consist of *ammono*-basic iodides is not convincing in the absence of analytical data for nitrogen. Although not extensive, the data given above indicate that in the normal laboratory atmosphere or in air saturated with water vapor, aluminum(III) iodide 6-ammoniate hydrolyzes to form mixtures of hydrates of NH_4I and $AlO(OH)$.

The assumption of the presence of significant concentrations of ammonium ion[5,6] in liquid ammonia solutions of aluminum(III) iodide is not necessary to account for the evolution of variable quantities of hydrogen[2,3,5,6] when potassium is added to such solutions at or below the boiling point of the solvent. If, for example, Al^+ is formed even transitorily, hydrogen could result from the reduction of ammonia

$$Al^+ + 2NH_3 \longrightarrow Al^{3+} + H_2 + 2NH_2^-$$

at a rate that precludes detection of reducing properties attributable to lower oxidation states of aluminum. This interpretation is entirely analogous to that given by Raijola and Davidson[21] for their inability to detect Al^+ formed in aqueous solutions. Their work together with that described above serves to render even more plausible the assumption of the transitory existence of lower oxidation states of aluminum in liquid ammonia solutions.[2]

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Molybdenum(V) and Molybdenum(VI) Complexes with Ethylenediaminetetraacetic Acid[1]

BY ROBERT L. PECSOK AND DONALD T. SAWYER

An investigation of polarographic methods for the determination of molybdenum has led to a study of the complexes of molybdenum(V) and (VI) with ethylenediaminetetraacetic acid (EDTA) and its salts. Continuous variations studies of the spectrum of the complexed molybdenum(V) indicated two molybdenums per EDTA in the complex. Solid chelates were synthesized and analyzed for the elements. All data support the proposal that these chelates contain a molar ratio of metal to EDTA of 2.0. The formulas are $Na_2Mo_2O_{12}H_{12}C_{10}N_2\cdot H_2O$ and $Na_4Mo_2O_{14}H_{12}C_{10}N_2\cdot 8H_2O$ for the (V) and (VI) oxidation states, respectively.

Many chelating agents are known to improve the nature of the polarographic wave for molybdenum(VI).[2] Since ethylenediaminetetraacetic acid and its salts (hereafter referred to as EDTA and designated H_4Y, H_3Y^-, H_2Y^{--}, HY^{-3} and Y^{-4}) are now commonly used as supporting electrolytes, it was of interest to investigate the nature of the molybdenum species present in these solutions. The results of a systematic study of the chelates formed between molybdenum(V) and molybdenum(VI) and EDTA are presented below. The composition of the chelates has been established by several independent methods. Structures have been proposed, together with electrode reactions which are consistent with the data.

Although the polarography of molybdenum(VI) has been studied extensively, most of the data pertain to solutions more acidic than *p*H 2.[2-11] The waves obtained are frequently complex and irreversible and, except for an interpretation of the change in oxidation state, very little is known concerning the nature of the complexes. The polarographic behavior of molybdenum(VI) in EDTA was reported briefly by two groups of investigators.[12,13]

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