aware are those of Roy, Hamill and Williams[9] in which I^- ions were used to scavenge I atoms that would otherwise react with I_2^- that they had been separated from by photochemical dissociation of I_3^-. The I_2^- was detected by oxidation of Mn^{++}, a scavenger that was present in too low concentration to affect recombination of original partners. The authors used a somewhat different treatment of the data, but their results gave approximately $d\phi/d[S]^{1/2} = 0.07$ (liter/mole)$^{1/2}$. If we use a for a diffusion controlled reaction for the recombination of $I + I_2^-$ from the original dissociation, and if we use

$$k_s = 4\pi\rho_s D_s N/1000 \tag{28}$$

where the subscripts refer to the scavenger reaction of $I + I^-$, then

$$\frac{d\phi}{d[S]^{1/2}} = \frac{2\sigma}{3\alpha}\left(\frac{8\pi\rho_s N D_s}{1000D}\right)^{1/2} \tag{29}$$

If $D_s = D$ (which means I^- and I_2^- have equal diffusion coefficients), and if $\rho_s = 4.3 \times 10^{-8}$ cm., then $\sigma/\alpha = 4 \times 10^{-9}$ cm. This small displacement distance would indicate a considerable tendency for original partners to recombine by diffusion and is consistent with the low quantum yields for dissociation compared to the quantum yields for dissociation of I_2 in hexane.[8] Also, combination of such a small displacement distance with the usual magnitudes of diffusion coefficients requires such frequent displacements that the molecules must be in almost continuous motion with no significant potential barrier opposing the diffusive motions that do occur. This conclusion is consistent with the observations of Watts, Alder and Hildebrand[10] on the temperature dependence of diffusion coefficients measured at constant volume.

Considerably more experimental work is needed before we can be sure of our interpretations, but data currently available do offer some encouragement that reasonable magnitudes of diffusive displacements are obtained by application of this model.

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NEW YORK 27, N. Y.

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[9] J. C. Roy, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **77**, 2953 (1955).

[10] H. Watts, B. J. Alder and J. H. Hildebrand, *J. Chem. Phys.*, **23**, 659 (1955).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Acidity of Catalyst Surfaces. I. Acid Strength from Colors of Adsorbed Indicators

BY H. A. BENESI

RECEIVED JUNE 25, 1956

Acid strength measurements of catalyst surfaces have been extended over a much wider range than that previously investigated. By noting the colors of adsorbed Hammett indicators useful information has been obtained regarding the effect of a variety of conditions on the acid strength of mounted acids, clays and cracking catalysts. It has been found, for example that: (1) the strength of an acid mounted on silica gel tends to increase with increasing acid concentration; (2) dried clays and cracking catalysts are still strongly acid after they have been "neutralized" with aqueous sodium hydroxide solution; (3) unused silica–alumina catalysts appear to be at least as strongly acid as 90% sulfuric acid; (4) silica–magnesia catalysts are weaker acids than silica–alumina catalysts.

The surface acidity of solid catalysts has been the subject of considerable study, yet its characterization remains far from complete. Although it has been shown that the centers giving rise to surface acidity can be strongly acid,[1,2] and that they occupy only a small fraction of the total catalyst surface,[3] little is known regarding the acid strength distribution among such centers and how this distribution varies with the type of catalyst. The present series of studies was undertaken to obtain such information.

As the first step, we used appropriate indicators (henceforth called Hammett indicators) to measure the acid strength of a variety of acidic catalysts following the simple method suggested by Walling.[2] This method consists of contacting separate samples of the solid under study with each indicator solution and noting the resulting colors of the adsorbed indicators. Upon carrying out such indicator tests, we were surprised to find that carefully dried samples of several of the solids studied gave acid colors with all available indicators, including anthraquinone—which is so weakly basic it requires a sulfuric acid concentration greater than 90 wt. % to convert it to its conjugate acid. This finding made it evident that the acidity of some surfaces is fantastically strong and that acid strength measurements could now be extended over a much wider range than that previously investigated. Although the differentiation between different acid strengths is quantized (the size of the quanta being determined by the difference in indicator pK_a's), it has been found possible to obtain useful information regarding the effect of a variety of conditions on the acid strength of mounted acids, clays and cracking catalysts.

Theory.—The acid strength of a solid surface is defined as its proton-donating ability, quantita-

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[1] H. Weil-Malherbe and J. Weiss, *J. Chem. Soc.*, 2164 (1948).

[2] C. Walling, THIS JOURNAL, **72**, 1164 (1950).

[3] G. Mills, E. Boedeker and A. Oblad, *ibid.*, **72**, 1554 (1950).

tively expressed by Hammett and Deyrup's H_0 function,[4] where

$$H_0 = -\log a_{H^+} f_B / f_{BH^+} \quad (1)$$

and where a_{H^+} is the hydrogen ion activity of the surface acid and f_B and f_{BH^+} are activity coefficients of the basic and acid forms, respectively, of the adsorbed indicator. In using H_0 as an acid strength index for solid surfaces the chief requirement that has to be satisfied is that the f_B/f_{BH^+} ratio for an adsorbed indicator be independent of the indicator used. Although this cannot be shown directly, the fact that the entire series of indicators used in the present study give self-consistent color reactions on solid surfaces shows that the f_B/f_{BH^+} ratio is either independent of the indicator used or varies in a regular manner with decreasing indicator basicity. This result is not surprising. The highly polar surfaces studied furnish localized media of high dielectric constant that can be considered two-dimensional analogies of a homogeneous medium like sulfuric acid, in which the f_B/f_{BH^+} ratio is known to be independent of the indicator used.

The acid strength definition embodied by equation 1 differs from that proposed by Walling[2] in one important respect. Walling suggested the use of a more general H_0 function that includes the activity of "Lewis acids" as well as hydrogen acids. However, Hammett and Deyrup's quantitative treatment of hydrogen acids simply is not applicable to "Lewis acids" because—as Lewis,[5] himself, pointed out—the relative strengths of generalized (Lewis) acids depend not only on the solvent medium but also upon the particular base used for reference. Thus, even if "Lewis acids" on a solid surface give rise to indicator color changes, the results could not be expressed in terms of a single H_0 function—each Lewis acid would have to be treated as an individual case. However, there is no reason to suspect that any of the color reactions reported in the present study are the result of a process other than proton transfer.

The restrictions that apply to the use of acid–base indicators in measuring acid strengths of solid surfaces are listed elsewhere.[2] One additional point should be mentioned. In most cases studied, only a small fraction of the surface is occupied by acid centers. Since it is this fraction that is of most interest, the color of the acid form of the indicators used must mask the color of the basic form.

The Hammett indicators used in the present study are listed in Table I, together with their color changes and pK_a's. To give some idea of the enormous acid strength range spanned by this bank of indicators, sulfuric acid compositions corresponding to the mid-point of each of the acid–base transitions are also listed.

The limits of the H_0 of a surface are established by observing the color of the adsorbed form of the Hammett indicators. As examples, a solid having an H_0 of -5.6 to -8.2 gives a yellow color with benzalacetophenone and gives no color with anthraquinone; a solid with an $H_0 < -8.2$ gives acid colors with all Hammett indicators.

TABLE I

INDICATORS USED FOR ACID STRENGTH MEASUREMENTS

Indicator	Basic color	Acid color	pK_a	H_2SO_4, % wt.
Neutral red	Yellow	Red	+6.8	8×10^{-8}
Phenylazonaphthylamine	Yellow	Red	+4.0	5×10^{-5}
Butter yellow	Yellow	Red	+3.3	3×10^{-4}
Benzeneazodiphenylamine	Yellow	Purple	+1.5	0.02
Dicinnamalacetone	Yellow	Red	−3.0	48
Benzalacetophenone	Colorless	Yellow	−5.6	71
Anthraquinone	Colorless	Yellow	−8.2	90

Experimental

Acid Strength Measurements.—Color tests were made by transferring roughly 0.1 g. of dried, powdered solid to a test-tube, adding 3–5 ml. of dry benzene, and then adding a 0.1% solution of indicator in benzene (four drops in the case of benzalacetophenone and anthraquinone, one drop in the case of the other indicators). From the results of such tests, it was easy to decide whether the solid under study was basic to all indicators, acid to all indicators, or had an H_0 lying between two adjacent indicator pK_a's.

Samples were subjected to color tests immediately after drying, or, if this was not convenient, were stored in screw cap bottles in a desiccator until color tests were made. Since water is a base, the effect of water adsorption was either to decrease color intensities of the absorbed indicators or to cause a shift to lower acid strengths. By carrying out parallel tests inside and outside a dry box, it was found that water adsorbed during a single transfer of dried sample to the test-tube had a negligible effect on acid strength.

Indicators.—All indicators used in the present study are Eastman Kodak (white label) products.

Neutral red (2-methyl-3-amino-6-dimethylaminophenazine) was obtained in the form of the hydrochloride salt. It was converted to the neutral base by adding a slight excess of standardized sodium hydroxide solution. The product was washed and then stored in a desiccator over Drierite for several weeks before using. The pK_a of neutral red was colorimetrically determined by Kolthoff.[6]

4-Phenylazo-1-naphthylamine was purified by recrystallization from cyclohexane. Its pK_a was determined spectrophotometrically by measuring absorption spectra of 4×10^{-6} *M* aqueous solutions over a wide *p*H range. The *p*H's were measured by means of a calibrated *p*H meter. The wave length at maximum optical density corresponding to the indicator base and its conjugate acid were found to be 4250 and 5400 Å., respectively. The pK_a found is $+4.00 \pm 0.05$.

Butter yellow (N,N-dimethyl-*p*-phenylazoaniline) was purified by recrystallization from isoöctane. Guntelberg and Schiodt[7] made a colorimetric determination of the pK_a of butter yellow.

Benzeneazodiphenylamine (4-phenylazodiphenylamine) was purified by recrystallization from petroleum ether. Its pK_a was colorimetrically determined by Hammett and Paul.[8]

Dicinnamalacetone (1,9-diphenyl-1,3,6,8-nonatetraen-5-one) was purified by recrystallization from a 1:1 mixture of benzene and isoöctane. Its pK_a (-3.0 ± 0.2) was determined spectrophotometrically[9] in sulfuric acid-water mixtures following a procedure very similar to that used by Hammett and Deyrup.[4] The accuracy of the pK_a determination is relatively low because sulfuric acid solutions of dicinnamalacetone are not stable, and because the extinction coefficients of the two forms of indicator may show a considerable drift over the wide range of sulfuric acid concentrations studied.

Benzalacetophenone and anthraquinone were purified by

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(4) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

(5) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(6) I. M. Kolthoff, *Rec. trav. chim.*, **43**, 144 (1924).

(7) E. Guntelberg and E. Schiodt, *Z. physik. Chem.*, **135**, 393 (1938).

(8) L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934).

(9) Determined by Dr. J. van der Waals.

recrystallization from isoöctane and benzene, respectively. Their pK_a's were determined by Hammett and Deyrup.[4]

Metal Oxides.[10]—Aluminum-free silica gel was prepared by precipitating the hydrogel from purified sodium silicate with dilute hydrochloric acid. The product was washed first with dilute acid and then with water, followed by drying at 120°. The sodium silicate had been purified by repeated precipitation and dissolution of the silica hydrogel, the hydrogel being washed with dilute acid at each stage.

Two alumina preparations were studied. The first was prepared by precipitation of aluminum hydroxide from aluminum nitrate using ammonium hydroxide. The second was prepared by hydrolyzing purified aluminum isopropylate. Both alumina preparations gave identical indicator tests.

Magnesia was prepared by precipitating magnesium hydroxide from magnesium chloride solution using ammonium hydroxide.

Mounted Acids.—Acids were mounted on pure silica gel (60 to 200 mesh) by an impregnation procedure. Enough 1 *M* acid was added to 10 g. of silica gel to give the desired acid concentration and enough distilled water added to the product to make a viscous slurry. The slurry was evaporated to dryness (with constant stirring) on a hot-plate and the product dried overnight at 120°.

Each of the resulting mounted acids had surface areas of approximately 500 m.^{2}/g. If one assumes that each of the acids studied has a covering power of *ca.* 35 A.^{2} per molecule, the fraction of the surface covered is about 0.04 for the 0.1 mmole/g. preparations and about 0.4 for the 1.0 mmole/g. preparation. It seemed reasonable to assume that the H_0 of a mounted polybasic acid represents the acid strength of the first ionizable hydrogen. Comparisons between mounted acids were therefore made on a molar rather than on a gram-equivalent basis.

Clays.—The montmorillonite clay used was a bentonite from Clay Spur, Wyoming, having a base-exchange capacity of 98 meq./100 g. of clay (dried at 120°). The amounts of the exchangeable cations in the original clay are as follows: 1.12% sodium, 0.35% potassium and 0.88% calcium. Pure sodium, ammonium and hydrogen montmorillonites were prepared by the method suggested by Lewis,[11] which consists of passing a dilute clay suspension through the appropriate form of Dowex-50 ion exchange resin. Subsequent chemical analyses of each of the above montmorillonites showed that ion exchange was complete in each case.

The kaolinite clay (trade name, Velvex) was obtained from Southeastern Clay Company, Aiken, South Carolina. Its base-exchange capacity was 2.5 meq./100 g. of clay. Pure sodium, ammonium and hydrogen kaolinites were prepared by successive washing with solutions of the appropriate ion form followed by extensive washing with distilled water.[12]

Each of the above clays was dried 16 hours at 120° before carrying out acid strength measurements.

Cracking Catalysts.—Most of the cracking catalysts studied are commercial products manufactured by Davison Chemical, American Cyanamid, Filtrol and National Aluminate Companies. Their compositions and physical properties have been listed by Ries.[13] The alumina–boria catalyst, which contained 12% B_2O_3, was prepared by impregnating alumina with boric acid using the method suggested by Bailey.[14] All cracking catalysts were calcined for at least 2 hours at 550° before carrying out acid strength measurements.

Results and Discussion

Metal Oxides.—To provide a frame of reference for studies of the surface acidities of mounted acids, clays and cracking catalysts, the Hammett indicators were applied to three metal oxide constituents of the above materials. These included silica gel, alumina and magnesia. Samples of these oxides were freshly dried at 120° before carrying out the indicator tests.

As was expected, the above oxides, when pure, do not show strongly acid properties. Alumina dried at 120° gives no acid colors with any of the Hammett indicators. Silica gel reacts acid to neutral red and basic to the remaining indicators thus giving an H_0 between +6.8 and +4.0. This low acid strength no doubt represents the inherent acidity of the silicic acid groups on the silica gel surface.

It is found that even traces of impurities can greatly increase the acid strength of the above oxides, the extent of the increase depending on the nature and amount of the acidic impurity. These results make it evident that the bright color of the acid form of the indicators used masks that of the basic form, even though the latter is the form predominantly adsorbed. In the case of commercially available alumina, the most troublesome impurities are silica, chloride and sulfate. In the case of silica gel, alumina and titania are the most common offenders.

It has been reported by Morton and Bolton[15] that strongly alkaline surfaces can cause indicators of the amino azo type to give virtually the same colors as those produced by strong acids. In agreement with their observations, we find that 4-phenylazo-1-naphthylamine and 4-benzeneazodiphenylamine are the only indicators used in the present study that give their "acid" colors on pure magnesia (calcined at 550°) and on sodium hydroxide That these color reactions are not truly produced by acid centers can be shown easily. The addition of *n*-butylamine instantly discharges the acid color if a surface is genuinely acidic; butylamine addition does not discharge the "acid" color produced by strongly alkaline surfaces.

Mounted Acids.—Several non-volatile acids were mounted on pure silica gel to give two acid concentrations. The acid strengths of the dried products are listed in Table II. In examining the data in this and the following tables it should be remembered that as H_0 decreases and approaches more negative values, the acid strength of the surface increases.

TABLE II

STRENGTH OF ACIDS MOUNTED ON SILICA GEL

Acid	H_0 0.1 mmole/g.	H_0 1.0 mmole/g.
H_3BO_3	+3.3 to +1.5	+1.5 to −3.0
H_3PO_4	+1.5 to −3.0	−5.6 to −8.2
H_2SO_4	−5.6 to −8.2	<−8.2
$HClO_4$	−5.6 to −8.2	−5.6 to −8.2

The results listed in Table II show, first, that the acid strengths at a dilute surface concentration are in the order $HClO_4 = H_2SO_4 > H_3PO_4 > H_3BO_3$. This order is identical with that found in dilute aqueous solution.

Second, the strength or hydrogen ion activity of mounted acids tends to increase with increasing concentration. An obvious analogy can be drawn between the behavior of the above two-dimensional systems and that observed in homogeneous

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(10) Prepared by Mr. W. E. Armstrong and Mr. L. B. Ryland.

(11) D. R. Lewis, *Ind. Eng. Chem.*, **45**, 1782 (1953).

(12) Pure forms of kaolinite were kindly furnished by Dr. D. R. Lewis.

(13) H. E. Ries, "Advances in Catalysis," Vol. IV, Academic Press, New York, N. Y., 1952, p. 88.

(14) W. Bailey, U. S. 2,377,744 (to Shell Development Company, June 5, 1945).

(15) A. A. Morton and F. H. Bolton, THIS JOURNAL, **75**, 1146 (1953).

media. Mounted perchloric acid does not show such an increase due, possibly, to differences between its geometrical distribution and those of the other acids, which are polybasic. In summary, the results shown in Table II are reasonable in the light of the known behavior of the acids studied. They therefore lend confidence in the use of indicator color changes to estimate acid strengths of "unknown" solid surfaces.

Clays.—All clays examined are strongly acid, especially after drying at 120°. Of the various classes of clays investigated thus far, the kaolins had the highest acid strength, the hydrated micas the lowest, while the strength of the montmorillonites and attapulgites fell in between. The above observations were made on samples of naturally occurring clays and should therefore be considered as tentative. Since the indicator tests are extremely sensitive and are a measure of the strongest acid centers, it is possible that acidic impurities or variations in the composition of the exchangeable cations can obscure the true acid strength of a pure clay fraction.

To obtain acid strengths of pure clay fractions, samples of a montmorillonite (Clay Spur, Wyoming bentonite) and kaolinite (Velvex) clay were converted to sodium, ammonium and hydrogen forms by ion exchange. The acid strengths of the dried products are listed in Table III.

TABLE III

ACID STRENGTH OF CLAY SURFACES

	H_0
Original Kaolinite	−3.0 to −5.6
Sodium Kaolinite	−3.0 to −5.6
Ammonium Kaolinite	−3.0 to −5.6
Hydrogen Kaolinite	−5.6 to −8.2
Original montmorillonite	+1.5 to −3.0
Sodium montmorillonite	+1.5 to −3.0
Ammonium montmorillonite	+1.5 to −3.0
Hydrogen montmorillonite	−5.6 to −8.2

As was expected, the measurements listed in Table III show that the acid strength of the hydrogen form of the above clays is higher than that of other forms. It is also evident that the sodium and ammonium forms of kaolinite are more strongly acid than the corresponding forms of montmorillonite. The surprising aspect of the above results is to find that clays whose cations have been "completely" replaced with ammonium or sodium ions from aqueous solution become strongly acid when the clay is dried! The reappearance of surface acidity upon drying can be explained in terms of a picture involving closely packed exchange positions in clays. According to this picture, all such exchange positions cannot be occupied because of steric hindrance (or electrostatic repulsion) between the highly solvated cations. Upon drying a "neutralized" clay at 120°, the solvation shell surrounding each cation is removed, thereby exposing other acidic exchange positions. If the resulting clay is reimmersed in water, its acidity disappears. This process is thus completely reversible provided the clay has not been dried at too high a temperature. Support for the above picture is provided in a later section where it is shown that the acidity of *all* dried clays can truly be neutralized by exposure to a volatile base such as ammonia or an amine.

Cracking Catalysts.—All solids so far examined that exhibit substantial hydrocarbon cracking activity have an H_0 less than +1.5. Cracking catalysts are thus strong acids, an observation that can be considered still another point in favor of the carbonium ion mechanism for catalytic cracking.

The acid strengths of the four well-known types of cracking catalysts are listed in Table IV. The results apply to commercial products as well as laboratory preparations provided they are pure. Silica–magnesia catalysts containing substantial amounts of alumina usually have a much higher acid strength than that indicated in Table IV.

TABLE IV

ACID STRENGTH OF CRACKING CATALYST SURFACES

Catalyst[a]	H_0
Silica–alumina (synthetic)	< -8.2
Natural clay catalysts	< -8.2
Alumina–boria	< -8.2
Silica–magnesia	+1.5 to −3.0

[a] Calcined 2 hours at 550°.

The data in Table IV show that the surface acidities of alumina–boria, silica–alumina and natural clay catalysts are so strong that all of the available Hammett indicators give their acid colors when adsorbed. On the other hand, silica–magnesia is mildly acid in comparison.

If one assumes that the coördination number of aluminum and magnesium is four in the above solids, the difference in acid strengths found is that predicted from the simple electrostatic rule suggested by Pauling.[16] According to this rule, each of the four oxygen atoms bonded to an aluminum atom retains a residual charge of $-^1/_4$ to hold the hydrogen counterion; oxygen atoms bonded to magnesium retain a residual charge of $-^1/_2$. Thus, tetrahedrally coördinated aluminum atoms in alumina–boria, silica–alumina and clay catalysts would be expected to impart a much higher acid strength than tetrahedrally coördinated magnesium atoms in silica–magnesia. It is not necessary, however, that *each* tetrahedral oxygen atom be bonded, in turn, to silicon atoms to form a three-dimensional network. In fact, under such circumstances the hydrogen counter ions would probably be buried and could not then contribute to surface acidity. The aluminosilicate structure postulated by Tamele[17] is a reasonable picture that explains the appearance of surface acidity in silica–alumina cracking catalysts.

Cracking catalysts can be sintered by heating to high temperatures *in vacuo*, by heating in the presence of steam and by commercial use in the refinery. The effect of the above three sintering treatments on the acid strength of silica–alumina catalyst is shown in Table V. All samples were originally Aerocat catalysts manufactured by the American Cyanamid Company.

(16) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 396.

(17) M. W. Tamele, *Faraday Soc. Disc.*, **8**, 270 (1950).

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.

Acknowledgment.—The author would like to express his gratitude to Dr. M. W. Tamele at whose suggestion the present field of study was undertaken and to Dr. J. N. Wilson for generous and helpful criticisms.

EMERYVILLE, CALIFORNIA

[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

RECEIVED MAY 17, 1956

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.

[2] G. W. Watt, J. L. Hall and G. R. Choppin, THIS JOURNAL, **73**, 5920 (1951); *J. Phys. Chem.*, **57**, 567 (1953).

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