TABLE II

CONSTANTS OF ELECTROLYTES IN ETHYLENE CHLORIDE

Salt	Λ_0	Λ_0^+	$K \times 10^4$
$(n\text{-}C_4H_9)_4NPi$[4]	57.40	26.2	2.28
$(n\text{-}C_4H_9)_4PPi$	57.27	26.1	1.60
$(n\text{-}C_4H_9)_4AsPi$	57.14	25.9	1.42
$(n\text{-}C_4H_9)_3SPi$	62.31	31.1	0.449
$(n\text{-}C_4H_9)_3SClO_4$	68.72	29.5	.394
$(C_6H_5)_2IPi$	62.50	31.3	.0233
$(C_6H_5)_2IClO_4$	70.42	31.2	.115

may well be due to the fact that the perchlorate is somewhat unstable as has been mentioned above.

The conductance of the tetra-*n*-butylammonium, phosphonium and arsonium ions shows a very slight decrease with increasing size of the central element. The dissociation constant of the picrates of these ions shows a marked decrease on going from the nitrogen to the arsenic derivative. The larger diameter of the heavier elements may provide a more open structure for the substituted groups and thus permit a closer approach of the picrate ion.

The sulfonium and iodonium ions, each possessing 12 carbon atoms, have almost the same conductance, 31.1 and 31.3, respectively. This indicates that, in ions of this type, the arrangement of the carbon atoms of the substituent groups has but little influence on conductance. It may be noted in this connection that the conductance of the tetra-*n*-propylammonium ion, also having 12 carbon atoms, is 31.4,[3] while that of the phenylpyridonium ion with two closely joined six-membered rings, is 36.7.[3]

A comparison of the dissociation constants of picrates of tetra-*n*-propylammonium,[3] tributylsulfonium, diphenyliodonium and phenylpyridonium ions, containing nearly the same number of carbon atoms, brings to light the influence of stearic factors on short-range ion-interactions. The dissociation constants for these picrates are, respectively, 1.94×10^{-4}, 0.44×10^{-4}, 0.023×10^{-4} and 0.86×10^{-4}.

The dissociation constant of the picrate of the sulfonium ion, with its planar structure, is only one-fourth that of the ammonium ion with tetrahedral structure. The constant of the picrate of the iodonium ion, with linear structure, is one-twentieth that of the corresponding salt of the sulfonium ion. The more open the structure of the cation, the nearer can the charge on the picrate ions approach the center of positive charge. In this connection, it is of interest to note that for phenylpyridonium picrate, the constant is nearly half that of tetrapropylammonium picrate and twice that of tributylsulfonium picrate. The phenylpyridonium ion is a small one, considering the number of atoms that it contains as evidenced by its high conductance. Although it bears some structural resemblance to the iodonium ion, its atoms are very closely packed as a result of which the negative ion is kept at a distance and the constant is relatively large.

V. Summary

1. Conductance measurements have been made with solutions of tetra-*n*-butylphosphonium picrate, tetra-*n*-butylarsonium picrate, tri-*n*-butylsulfonium picrate and perchlorate and diphenyliodonium picrate and perchlorate in ethylene chloride at 25°.

2. The limiting conductances and dissociation constants for these salts have been evaluated.

3. It has been found that the size of the central atom of these large quaternary onium ions has little influence on the ion conductances. The dissociation constant of their picrates decreases somewhat with increasing size of the central atom.

4. While the arrangement of a given number of carbon atoms around the central atom has but a small effect on ion conductance, it plays a major role in determining the value of the dissociation constant of the ion-pair equilibrium.

PROVIDENCE, R. I. RECEIVED NOVEMBER 15, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Reactivity of Hydrous Alumina toward Acids[1]

BY RONALD P. GRAHAM[2] AND ARTHUR W. THOMAS

Introduction

Although the reactivity of hydrous alumina toward aqueous solutions of acids has been the subject of a number of studies, the phenomena exhibited are not yet clearly understood. The literature of the last hundred years contains an appreciable amount of factual information, but it is only recently that attempts have been made to explain the results of study in an integrated manner.

An early observation was that freshly precipitated gelatinous hydrous oxide is readily peptized to the colloidal condition by the action of certain acids. It has been found, for example, that hydrochloric and acetic acids are effective in this respect whereas sulfuric and phosphoric acids are not good peptizing agents. Thomas and Vartanian[3] made an extensive study of the relative

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(1) Part of a Dissertation submitted in 1942 by Ronald Powell Graham in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

(2) Present address: Department of Chemistry, McMaster University, Hamilton, Ontario.

(3) Thomas and Vartanian, THIS JOURNAL, 57, 4 (1935).

amounts of colloidal and crystalloidal aluminum micelles or ions, respectively, resulting from the interaction of powdered hydrous alumina with various acids. They explained their findings on the basis of a coördination mechanism of peptization and dissolution. The results of this investigation have also been interpreted in the phraseology of the adsorption theory of peptization.[4]

The sorption of arsenious acid by alumina precipitated by aqueous ammonia from an aluminum salt has been investigated,[5,6] and the activity of the sorbent found to vary with the temperature of its preparation. A potentiometric investigation[7] has shown sulfuric and phosphoric acids to be sorbed to a greater extent than hydrochloric acid by alumina gel. In some investigations[6,8] of the sorption of certain acids by precipitated alumina gel and by hydrous alumina powder, the interference of dissolved aluminum ion in the titration procedure used for determining the sorption of acid has not, unfortunately, been properly considered.

The dissolution of "aluminum hydroxide" in hydrochloric acid containing certain alkali salts was studied by Tartar, Bryan, and Shinn.[9] The claim of these authors that the effects observed were due to the adsorption of anions of high valence at the solid–liquid interface is not in accord with the results of work by Clay and Thomas.[10] When studying the catalytic effect of anions upon the rate of dissolution of hydrous alumina powder by acids, these investigators found the rate-determining factor to be chemical in nature, and an explanation was offered based on a coördination structure of the hydrous oxide and the formation of a complex at the solid–liquid interface.

Developed upon the Werner–Pfeiffer ideas of hydrolysis and olation, and the process of oxolation, the concept of hydrous alumina as a coördinated structure with $\mathrm{Al{-}\overset{H}{O}{-}Al}$ and Al–O–Al linkages has been proposed,[3,10] and the viewpoint found a most fruitful one in interpreting studies with hydrous oxides and oxide hydrosols.[11] With respect to this structure, it is interesting to note that studies[12,13] on lepidocrocite (γ-FeOOH) have shown that it contains oxygen atoms of two kinds. Those of one type are bonded to iron atoms only, whereas each of the second kind is linked to two iron atoms and to two hydrogens. There is evidence[12,13] that the structure of böhmite (γ-AlOOH) is similar to that of lepidocrocite.

In the present research the neutralization of various acids by hydrous alumina has been investigated. The results of the study are related to the concept of hydrous alumina as a poly-olated and partially oxolated structure, and to the viewpoint that acids most reactive with it are expected to be those whose anions show a strong tendency toward complex formation with aluminum.

Experimental

Materials and Methods

Preparation of Hydrous Alumina.—Cleaned aluminum ingots,[14] weighing approximately 200 g. each, were amalgamated by immersing them in 5% aqueous mercuric chloride solution for three minutes. After rinsing in distilled water, the amalgamated specimens were used for the preparation of hydrous alumina as noted below.

Sample "26."—Thirteen batches of alumina were prepared as follows: Four amalgamated ingots were placed in three liters of distilled water at 26 ± 3° and after a reaction period of twenty-four hours the ingots were removed and the suspension stirred for a further period of twenty-four hours. The suspension was then filtered, spread on a glass plate, and allowed to dry for nine weeks at 25.0 ± 0.3°. During the drying period the mixed lots were pulverized from time to time to reduce the grain size to below 42-mesh and, before bottling, the powder was ground in an agate mortar to pass a 100-mesh sieve. A portion of this sample was mechanically screened to separate the −170 fraction. The analysis of both this latter material and of the −100-mesh powder can be expressed as equivalent to $Al_2O_3{\cdot}3.05H_2O$.

Sample "60."—Four batch lots of alumina were prepared in a manner similar to the above at a temperature of 60 ± 2°, the reaction time, with stirring, being six hours. After removal of the aluminum, the agitation was continued for twenty-four hours, the temperature meanwhile being allowed to fall to that of the room. The batches, after filtering, were mixed, and dried as above for twelve weeks during which time the sample was ground in agate to −42 mesh material. Later, a −115/+170 fraction was separated; this material analyzed to a composition equivalent to $Al_2O_3{\cdot}2.72H_2O$.

Sample "95."—The procedure for six batches was the same as for sample "60," except that the reaction temperature was 95 ± 2°, and the drying period eleven weeks. The sample was fractionated by mechanical screening, the analyses of the −42/+60, −115/+170, and −325 fractions being, respectively, $Al_2O_3{\cdot}2.62H_2O$, $Al_2O_3{\cdot}2.68H_2O$ and $Al_2O_3{\cdot}2.65H_2O$.

The composition of the hydrous alumina samples, expressed as above, was determined gravimetrically by ignition, in duplicate or triplicate. Appropriate testing of the samples for mercury showed that this element, if present (as a result of the amalgamation procedure), was in a concentration below the limit of detection (0.03%) of the *s*-diphenylcarbazide test.

Acid Solutions.—The acids employed were analyzed grades meeting A. C. S. specifications.[15] Solutions were standardized, using phenolphthalein, against carbonate-free sodium hydroxide; the latter was standardized by means of potassium acid phthalate from the National Bureau of Standards. When the acid normality is referred to below as 0.1 or 0.2 *N*, it is to be understood that

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[4] Weiser, "Inorganic Colloid Chemistry," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1935, p. 108–109. This work (pp. 107–108) furnishes references to much of the earlier work on the peptization of hydrous alumina by acids.

[5] Yoe, THIS JOURNAL, **46**, 2390 (1924).

[6] Sen, *J. Phys. Chem.*, **31**, 686 (1927).

[7] Berestneva and Kargin, *J. Phys. Chem.*, U. S. S. R., **13**, 1625 (1939); through *C. A.*, **35**, 362 (1941).

[8] Dewey, *J. Phys. Chem.*, **36**, 3187 (1932).

[9] Tartar, Bryan and Shinn, THIS JOURNAL, **55**, 2266 (1933).

[10] Clay and Thomas, *ibid.*, **60**, 2384 (1938).

[11] Thomas, "Colloid Chemistry," McGraw-Hill Book Company, New York, N. Y., 1934, Chapter VII, and later work by Thomas and co-workers in THIS JOURNAL.

[12] Bernal and Megaw, *Proc. Roy. Soc.* (London), **151A**, 384 (1935).

[13] Ewing, *J. Chem. Phys.*, **3**, 420 (1935).

[14] Obtained from The Aluminum Company of America and specified as 99.85% pure.

[15] Except sulfamic acid, which was a recrystallized product obtained through the courtesy of Dr. H. C. Beachell of the du Pont Company.

the determined normality was within ±0.2% of 0.1000 or 0.2000 *N*, and known with a precision of better than ±0.1%.

Measurement of Rate of Solution.—A weighed quantity of the hydrous alumina was transferred to a 250-ml. Non-Sol bottle, and there was added the desired quantity of standard acid at the appropriate temperature. After sealing the stopper, the bottle was revolved at 12 r. p. m. in a bath maintained within ±0.01° of the desired temperature.

At the expiration of a suitable time interval, eight drops of a saturated (at room temperature) solution of sodium sulfate were added to precipitate colloidally dispersed alumina, and the contents of the bottle transferred to an 100 ml. conical-base centrifuge tube. After centrifugation, approximately-sized samples of the clear supernatant liquid were pipetted for analysis, and the acid content determined (in duplicate, with a precision of ±0.2%) by a method described elsewhere.[16] Paraffined containers were used in the runs employing hydrofluoric acid.

Experimental Results

Reactivity toward Various Acids.—The reactivity of a number of acids with hydrous alumina sample "26" (−100-mesh) is shown in Fig. 1. In each case there were present 523 mg. of hydrous alumina (equivalent to 340 mg. of aluminum oxide) initially, and 100.0 ml. of the aqueous acid solution. The acid solutions were 0.2 *N* (the phosphoric acid was 0.1 *M*), and the reactions were carried out at 25°.

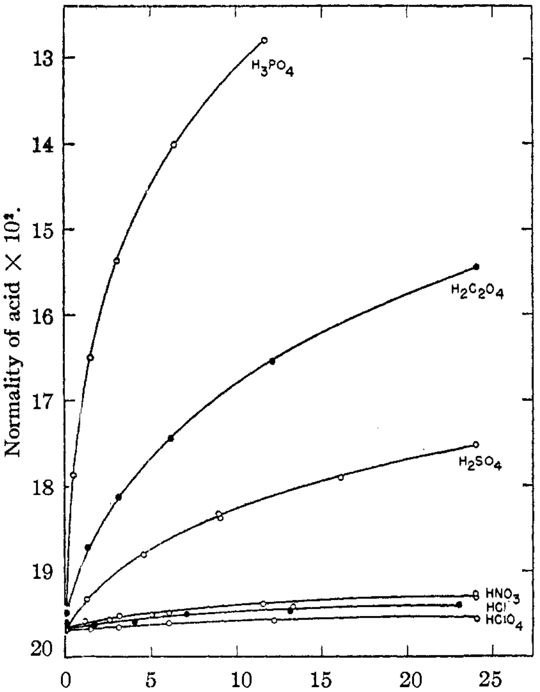

Fig. 1.—Reactivity of alumina "26" toward various acids

The reaction with hydrofluoric acid was too rapid for plotting on the scale used in Fig. 1, the normality of this acid having decreased to approximately 0.01 in less than half an hour. Some experiments with sulfamic acid indicated that its curve was immediately adjacent to that of hydrochloric acid.

Rapid Initial Neutralization Effect.—In order to investigate further the apparent lack of continuity with the origin in the case of the curves for the less reactive acids, a series of experiments was undertaken with measurements confined to the initial portions of the curves. In this series—using alumina "95"—the acid, its concentration, the temperature of the reaction, and the mass of alumina taken were varied.

In the lower group of four curves of Fig. 2, sulfuric, hydrochloric, perchloric and acetic acids, all at 0.2 *N*, were allowed to react at 25° with alumina in the ratio of 499 mg. of the latter to 100.0 ml. of the acid. In the next series, using 998 mg. of hydrous alumina and 50.0 ml. of acid, the curves for 0.1 *N* sulfuric acid at 15 and 25° are compared, as are also the results with 0.2 and 0.1 *N* sulfuric acid, both at 25°. The conditions for the two upper curves were as labeled, together with the data that 50.0 ml. of acid was used with 1.965 g. of sample in the lower of these curves, and with 3.493 g. in the upper one.

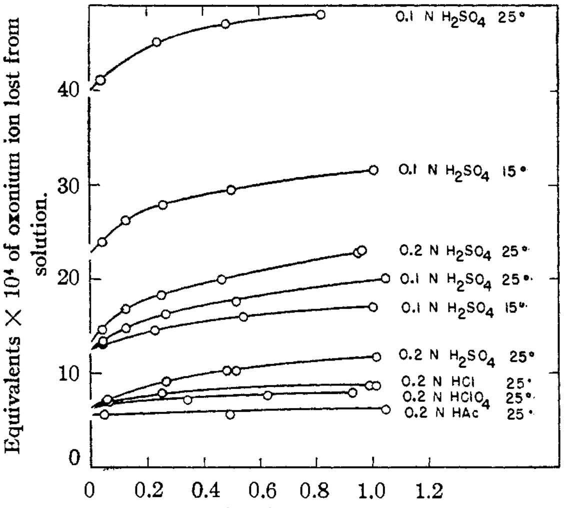

Fig. 2.—Initial effect, with alumina "95."

It was found that with acids effective in the formation of colloidal alumina, *e. g.*, perchloric and hydrochloric acids, the amount of dispersed alumina in the case of runs with sample "95" was very much greater than in the case of those with alumina "26" (corresponding experiments of Fig. 1 data).

Dependence of "Initial Effect" on Surface.—Each curve in Fig. 2 appears to extrapolate to a value on the ordinate which, within the precision of the data, is independent of the acid, its temperature or concentration, but is a function of the amount of alumina used. The linearity existing between the extrapolated values and the mass of alumina is shown in Fig. 3.

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(16) Graham, *Ind. Eng. Chem., Anal. Ed.*, **18**, 472 (1946).

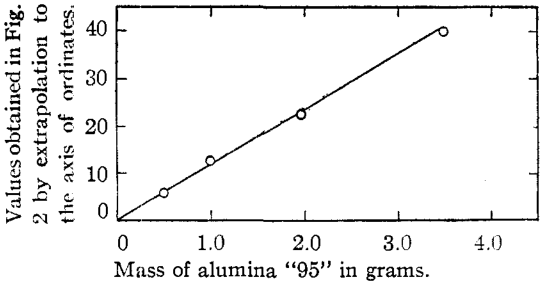

Fig. 3.—Dependence of initial effect on surface area.

Effect of Mesh Size on Reactivity.—The possible dependence of the reactivity of alumina on its sieve mesh size was studied using the screen sizes −42/+60, −115/+170, and −325, of sample "95." Quantities of this alumina, equivalent to 340 mg. of aluminum oxide, were treated with 100.0 ml. portions of 0.2 *N* sulfuric acid, and the reaction at 25° followed for several hours (Fig. 4).

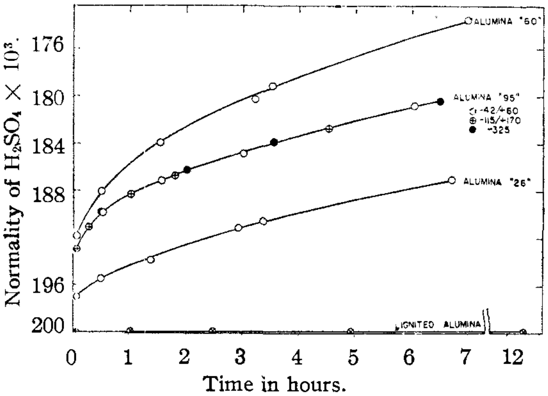

Fig. 4.—Reactivity at 25° of alumina samples prepared at different temperatures.

Effect of Temperature of Preparation on Reactivity of Alumina.—In Fig. 4, in addition to the curves for various screen sizes of alumina sample "95," there are plotted curves for alumina "60" (−115/+170), for sample "26" (−170), and for ignited alumina, obtained under the same conditions as the just previously noted "95" runs.

Although it is evident from Fig. 4 that the order of reactivity of the hydrous aluminas, insofar as the "initial effect" is concerned, is "60" > "95" > "26," it cannot be assumed that this is the order of reactivity of the aluminas as regards their dissolution in the acid. To determine the relative rates of dissolution of the aluminas in excess acid, a number of experiments were carried out with the results shown in Table I.

The reactivity of the aluminas, as measured by rate of dissolution, is in the order "26" > "60" > "95."

TABLE I

TIMES FOR COMPLETE DISSOLUTION OF ALUMINAS IN SULFURIC ACID

Hydrous alumina sample Treatment	"26"	"60"	"95"
Hydrous alumina equivalent to 680 mg. of Al_2O_3 boiled under reflux with 100.0 ml. of 1 *M* H_2SO_4	37 min.	47 min.	Not detd.
Hydrous alumina equivalent to 680 mg. of Al_2O_3 boiled under reflux with 100.0 ml. of 0.5 *M* H_2SO_4	85 min.	117 min.	166 min.
Hydrous alumina equivalent to 340 mg. of Al_2O_3 agitated at 25° with 100.0 ml. of 1 *M* H_2SO_4	29 days	69 days	122 days

Temperature Coefficient of Reaction.—In order to investigate the temperature coefficient, 249 mg. samples of alumina "95" (−325 mesh), equivalent to 170 mg. of aluminum oxide, were allowed to react with 100.0 ml. of 0.1 *N* oxalic acid at 15, 25 and 35°. The data obtained in these runs are plotted in the accompanying Fig. 5. The temperature coefficient for each of the ten degree intervals is 1.9 for the reaction subsequent to the "initial effect."

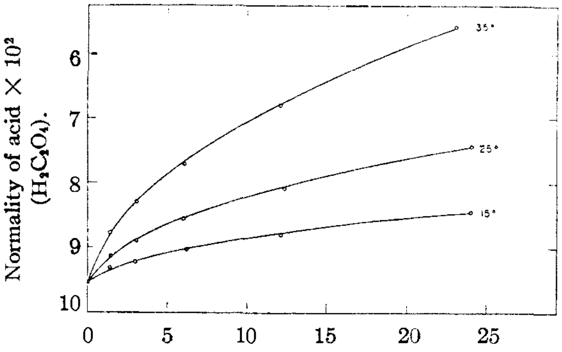

Fig. 5.—Reactivity of alumina "95" with varying temperature of reaction.

Effect of Stirring on Rate of Reaction.—The reactivity of colloidally dispersed alumina with acid was found not to depend on the degree of agitation. Using perchloric acid and hydrous alumina "95," parallel experiments were undertaken, in one of which the mixture was agitated as usual, whereas in the other the container was clamped rigidly in the thermostat after the addition of the acid, which dispersed essentially all the alumina to the colloidal state. Analysis of the solutions after an interaction period of one hour showed the residual acid normality to be the same in each case.

Discussion

This investigation furnishes very definite experimental evidence that there are, as postulated by Clay and Thomas,[10] at least two stages in the reaction of acids with hydrous alumina. Prior to a slower loss of oxonium ions from the solution, there is a comparatively rapid "initial effect" as is shown in the case of the less reactive acids by the curves being non-continuous with the origin (Fig. 1 and especially Fig. 2).

The extent of the initial effect would be expected to be independent of the acid used (as it is) if the reaction was due to the conversion, by means of oxonium ions, of hydroxo groups on the surface of the hydrous alumina to aquo groups, since this reaction should not involve anions. If the initial loss of oxonium ion is caused by the presence of hydroxo groups on the oxide surface, then the extent of the reaction, when expressed in terms of equivalents of oxonium ion lost from solution, should be independent of the initial concentration of the acid. Evidence that this is the case is given in Fig. 2 by the results with 0.2 and 0.1 *N* sulfuric acid at 25° with a constant quantity of hydrous alumina.

Further, hydroxo group neutralization would be expected to occur instantaneously, and thus such a reaction would appear temperature independent at ordinary temperatures in terms of the time scale imposed by the technique of experimentation. Such a result obtains as shown by the data for 0.1 *N* sulfuric acid at 15 and 25° in Fig. 2, and the results with 0.1 *N* oxalic acid at 15, 25 and 35°, in Fig. 5. In addition, the extent of the reaction due to hydroxo groups should vary linearly with the mass of alumina used. That such a relationship exists is shown in Fig. 3.

It is seen from Figs. 1 and 2 that perchloric and acetic acids react with alumina at similar slow rates, whereas phosphoric acid and especially hydrofluoric acid react at comparatively rapid rates. The reaction rates for the various acids are not in the order of their oxonium ion activities, nor of the valences of their anions.[9]

Evidence contra-indicating that diffusion factors are of primary importance in the reactions is furnished by the temperature coefficient. The average coefficient of reactions limited by diffusion is about 1.25,[17,18] the value (1.9) for the reaction studied in this work is indicative of a chemical process in the rate-determining step. Further, oxalic, sulfuric and phosphoric acids react with alumina much more rapidly than do hydrochloric and nitric acids, whereas the latter acids have the higher diffusion coefficients.[19] When diffusion is the predominant factor, the rate of reaction is dependent on the rate of stirring.[20] It has been shown that the rate of reaction of perchloric acid with hydrous alumina is independent of the degree of agitation. These lines of evidence indicate that the diffusion theory of heterogeneous reactions is not applicable to the present study.[21]

An explanation of the data for the several acids is found by considering the tendencies of the anions to form coördination compounds with aluminum. The hexafluoaluminate, $AlF_6^{\equiv}$, and trioxalatoaluminate, $Al(C_2O_4)_3^{\equiv}$, complexes are well known. The stability and rapidity of formation of fluorido and oxalato complexes of aluminum are evidenced by their use to eliminate the interference of this element in the determination of free acid in aluminum salts[16] and in other analytical procedures. Also, phosphato[22,23] and sulfato[24] aluminum complexes are known. On the other hand, the chlorido complexes of aluminum in aqueous solution are not stable ones,[25] perchlorate ion shows but little tendency toward complex formation,[26,27] and no nitrato- or normal acetato–aluminum complexes appear to have been described.[28]

The reactions occurring may be postulated as follows: After the immediate conversion of surface hydroxo groups into aquo groups by oxonium ions of the acid, the reaction proceeds by way of an anion mechanism. The tendency of the anions, in particular good complex-forming ions, to bind coördinatively to aluminum results in the rupture of the oxide structure by the breaking of ol and oxo linkages, oxonium ions neutralizing the hydroxo groups produced. The reaction may be regarded, in the nomenclature of Hammett,[29] as a nucleophilic displacement on aluminum, with the energy of formation of the aluminum-anion complex being to a certain extent utilized in disrupting the aluminum-ol and -oxo linkages. That such a displacement reaction occurs is strongly suggested by the correspondence existing between the rate of reaction and the stability of the aluminum-anion complexes.[30]

The conversion of all the basic groups in the hydrous alumina structure to water or aquo groups would require the complete dissolution of the oxide with all the aluminum converted into the crystalloidal condition. A study of the dissolution of hydrous alumina in acid as measured

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(17) Taylor, "A Treatise on Physical Chemistry," Vol. II, D. Van Nostrand Company, New York, N. Y., 1932, p. 1026.

(18) Moelwyn-Hughes, "The Kinetics of Reactions in Solution," The Clarendon Press, Oxford, 1933, p. 273.

(19) "International Critical Tables," Vol. V, McGraw-Hill Book Company, New York, N. Y., 1926, p. 63.

(20) King and Braverman, THIS JOURNAL, **54**, 1744 (1932).

(21) *Cf.* the view (20) that "In the case of metallic oxides . . . dissolving in acids, we should expect the chemical reaction to be so fast that the observed rate of solution would be controlled by the diffusion process."

(22) Bjerrum and Dahm, *Z. physik. Chem.*, Bodenstein Festband, 627 (1931).

(23) Jensen, *Z. anorg. allgem. Chem.*, **221**, 1 (1934).

(24) Spacu and Popper, *Bull. soc. Stiinte Cluj*, **8**, 5 (1934); through *C. A.*, **29**, 1027 (1935).

(25) Thorne and Ward, "Ephraim's Inorganic Chemistry," Gurney and Jackson, London, 1939, pp. 300–301.

(26) Hammett, "Solutions of Electrolytes," McGraw-Hill Book Company, New York, N. Y., 1936, p. 126.

(27) Rabinowitch and Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(28) Refractometric evidence for the existence in aqueous solution of the basic complex ion $Al_3(CH_3COO)_6(OH)_2^+$ has been obtained by Spacu and Popper, *Kolloid-Z.*, **103**, 19 (1943).

(29) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 142.

(30) Ref. 29, pp. 136–137.

by analyses for crystalloidal aluminum ions[10] could not, of course, detect the previously discussed initial reaction of the acid. The latter reaction with hydroxo groups is a step in the dispersion of alumina to the colloidal state[3]; this peptization reaction requires oxonium ion, but does not produce crystalloidal aluminum ions. Nevertheless, insofar as the same acids were used, the relative rates of neutralization of the acids (subsequent to the "initial effect") are found in this investigation to be almost identical, qualitatively, with the relative rates of dissolution of hydrous alumina by the acids.[10] This is to be expected because both processes depend on the same anion reactions.

On the basis of the present work it might be expected that the catalytic effect of hydrous alumina on the rate of hydrolysis of esters of the same alcohol would be in the order of the rates of neutralization of the respective acids by hydrous alumina. Some preliminary experiments were carried out using methyl oxalate and methyl iodide in aqueous solution in the presence and absence of a quantity of a sample of hydrous alumina. In the case of methyl oxalate, the rate of hydrolysis in the presence of the hydrous oxide was 2.1–2.5 times the rate of the reaction in pure water, whereas the factor for the catalyzed reaction with methyl iodide was only 1.1–1.2. Since it is fair to assume that the rate of neutralization of hydriodic acid by alumina would be far slower than that of oxalic acid, and closely similar to that of hydrochloric acid in view of other work in this Laboratory[31] on the relative effects of chloride and iodide ions on hydrous alumina micelles, the results are thus in accord with the expectation.

From the observation (which, it may be noted, was confirmed in the present work) that alumina prepared at an elevated temperature was more readily dispersed colloidally than one prepared at room temperature, it has been assumed[10] that the more reactive sample possessed more hydroxo groups on the surface. The data in Fig. 4 indicate that aluminas "60" and "95" are richer in surface hydroxo groups than sample "26" which was prepared at room temperature. Confirmatory evidence was furnished by adding small amounts of aluminas "26," "60" and "95" separately to 1 ml. quantities of a 1% solution of phenolphthalein in purified 1,4-dioxane; it was found that the surface of aluminas "60" and "95" immediately turned red, whereas that of alumina "26" became only faintly pink.

The extent of surface hydroxo groups of the hydrous alumina samples is not in the order of the temperatures of preparation of the oxides, since the curve (Fig. 4) for alumina "60" lies above that for sample "95", although both possess more hydroxo groups than alumina "26." This suggests that with increased heating of hydrous alumina in aqueous suspension, the number of surface hydroxo groups increases to a maximum, and then decreases to become zero in the case of ignited alumina. The latter oxide, as is to be expected, showed no "initial effect" (Fig. 4), and, similarly, remained pure white in the previously-described phenolphthalein test.

The reactivity of hydrous alumina as regards the complete breakdown of its structure by dissolution in acid should, however, continuously decrease with increasing temperature of preparation due to the resultant increased oxolation. That this is so is evident from Table I together with the data of Fig. 4 relating to the extreme inertness of ignited alumina. The latter may be considered as possessing a completely oxolated structure.

It is clear from Fig. 4 that the reactivity of hydrous alumina "95" is independent of its screen size. This suggests that the variously-sized particles broke down in the acid solution to closely the same size. That most extensive fragmentation occurs immediately was revealed by treatment of individual particles of alumina with acid while they were under microscopic observation. The larger particles are evidently conglomerations of much smaller fragments, loosely held together.

Acknowledgment.—The authors wish to express their appreciation for the interest and helpful suggestions of Dr. Leon Greenstein.

Summary

The reaction of acids with hydrous alumina occurs in at least two steps, the initial one being attributed to a rapid conversion, by oxonium ions, of surface hydroxo groups into aquo groups. Evidence is furnished that the subsequent slower reaction of the acid does not depend primarily on a diffusion phenomenon, but rather upon deolation of the oxide structure by the anion of the acid, such deolation being related to the tendency of the anion to form complex compounds with aluminum.

The catalytic effect of hydrous alumina on the hydrolysis in water of methyl oxalate and of methyl iodide is found to be in the order of the rates of reaction of the resultant acids with alumina.

The reactivity of hydrous alumina as regards complete dissolution in acids has been shown to decrease with increasing temperature of preparation of the oxide, the effect being ascribed to increasing oxolation of the alumina structure. Evidence is presented that, with increasing temperature of preparation, the number of surface hydroxo groups passes through a maximum, and becomes zero in the case of ignited alumina.

NEW YORK, N. Y. RECEIVED SEPTEMBER 3, 1946

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[31] Thomas and Whitehead, *J. Phys. Chem.*, **35**, 27 (1931).