[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Catalytic Effect of Anions upon the Rate of Dissolution of Hydrous Alumina by Acids

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The effect of certain acids in aqueous solution—hydrobromic, hydrochloric, nitric, sulfuric, oxalic, hydrofluoric, phosphorous and phosphoric—upon the rate of dissolution of certain hydrous alumina specimens has been found by the writers to vary greatly with the nature of the anions of the acids. The first four acids mentioned above are extraordinarily less active in the dissolution of aged hydrous alumina than the latter four, despite the fact that the former have greater activity and diffusion coefficients.

These effects, reported herein, are not in accord with the classical theory[1] that the rate-determining factor in reactions at a solid–liquid interface is the rate of diffusion of the reactants into a film of a saturated solution of the solid at the interface and of the product away from this film.

Neither are the observations reported herein in accord with the hypothesis[2] that anions of high valence will increase the velocity of dissolution of hydrous alumina in acid solutions, owing to adsorption of these anions at the solid–liquid interface and to concomitant lowering of the potential difference at this interface.

The present results indicate that the rate-determining factor is chemical in nature, and the writers submit an explanation involving the formation of a complex at the solid–liquid interface.[3]

Materials

Amalgamated Aluminum.—Aluminum ingots[4] were amalgamated by placing them in contact with redistilled mercury in a 5% aqueous solution of mercuric chloride. When the surface of the aluminum was covered with mercury the ingots were washed free of electrolyte with hot distilled water and were kept under distilled water at room temperature until needed.

Hydrous Alumina.—The specimens of hydrous alumina used in this investigation were prepared in the following manner.

Specimen "A."—Twelve pieces of amalgamated aluminum weighing approximately 200 g. each were placed in two liters of distilled water at 25 ± 2° and allowed to react for twenty-four hours. The suspension was filtered and dried in air at room temperature, pulverized to a fine powder, and allowed to remain in contact with the atmosphere until it showed no change in water content on three successive days. This procedure was continued until 1000 g. of oxide was obtained. The oxide was then thoroughly mixed and screened through a 100-mesh sieve. This specimen showed upon analysis the composition $Al_2O_3 \cdot 2.89 H_2O$.

Specimen "B."—The procedure was the same as for Specimen "A" except that the amalgamated aluminum was placed in boiling water and allowed to react at this temperature for six hours. This specimen showed upon analysis the composition $Al_2O_3 \cdot 2.70H_2O$.

Acids.—The acids used were reagent grade and the acid solutions were prepared by quantitative dilution of solutions which had been standardized by means of carbonate-free sodium hydroxide solution. The latter was standardized against acid potassium phthalate.

Measurement of the Rate of Solution.—A weighed quantity of the hydrous oxide was transferred through a funnel into a 300-ml. flint glass bottle by means of 200 ml. of the acid solution of the desired concentration. The bottle was placed in a motor-driven rotator which revolved at the rate of seven r. p. m., in a water-bath at 25 ± 0.05°. At the expiration of the desired time of rotation the contents of the bottles were poured into centrifuge tubes. One drop of a saturated solution of ammonium sulfate was added to solutions of Specimen "A" and five drops to solutions of Specimen "B" in order to precipitate colloidally dispersed alumina. The bottles were then centrifuged for ten minutes at 1500 r. p. m. (rotating radius to middle of tube was 42 cm.). After centrifuging, the supernatant liquor was siphoned off and appropriate quantities taken for analysis.

Waxed bottles were used whenever hydrofluoric acid was present.

Methods of Analysis

Three methods of analysis for aluminum were used in this investigation: (I) in the presence of phosphate and phosphite, (II) in the presence of oxalate and (III) in the presence of fluoride, sulfate, chloride, bromide and nitrate.

For (I) aluminum in the presence of phosphate, phosphite and pyrophosphate the method of Hillebrand and Lundell was used.[5a] The pyrophosphate was hydrated[6] to the phosphate by addition of hydrochloric acid to 2 *M* strength and by boiling for three hours.

In the presence of sulfate, chloride, fluoride, bromide, and nitrate (II) the aluminum was precipitated as the hydroxide, according to the method of Blum,[7] and ignited

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[1] (a) Noyes and Whitney, *Z. physik. Chem.*, **23**, 689 (1897); (b) Nernst, *ibid.*, **47**, 52 (1904); (c) Nernst and Brunner, *ibid.*, **47**, 56 (1904).

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

[3] Schwab, Taylor and Spence, "Catalysis," D. Van Nostrand Company, Inc., New York, N. Y., 1937, p. 219.

[4] The aluminum, specified as 99.94% pure, was obtained from The Aluminum Company of America.

[5] (a) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 399; (b) *ibid.*, p. 394.

[6] Kiehl and Claussen, THIS JOURNAL, **57**, 2284 (1935).

[7] Blum, *ibid.*, **38**, 1282 (1916).

and weighed as Al_2O_3. Since the maximum concentration of fluoride in any determination was 0.008 molar, its presence did not cause an appreciable incomplete precipitation of aluminum. In all cases, treatment of the aluminum oxide residue with hydrofluoric acid, followed by evaporation and re-ignition,[5b] caused no loss in weight, indicating the absence of an appreciable quantity of silica.

In the presence of oxalic acid (II) the solution was evaporated almost to dryness, cooled and treated with 5 ml. of concentrated sulfuric plus 5 to 10 ml. of concentrated nitric acids. After heating for two hours on a steam-plate to oxidize completely the oxalic acid, the aluminum content was determined as in method III.

Analyses for aluminum in the presence of chloride, bromide, sulfate, nitrate and oxalate were also made by precipitation, as the phosphate. Such analyses showed that when aluminum is precipitated as the phosphate the results are consistently 2–3% higher than when the aluminum is precipitated as the hydroxide. Therefore the results of all analyses for aluminum precipitated as the phosphate were lowered by 3%.

It was also found to be necessary to oxidize the oxalate with nitric acid before precipitating the aluminum phosphate.

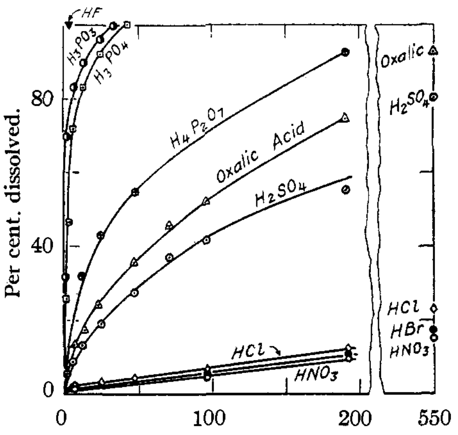

Fig. 1.—The dissolution of $Al_2O_3 \cdot 2.89H_2O$ in diverse acids. This graph contrasts the rates of dissolution of 260 mg. of 100-mesh $Al_2O_3 \cdot 2.89H_2O$ at 25° in 200 ml. of 0.2 N solution (H_3PO_3 and H_3PO_4 were 0.1 M) of the acids indicated on the curves.

Experimental Results

The curves for the dissolution of Specimen "A" in 0.2 N solutions of hydrofluoric, phosphorous, phosphoric, oxalic, sulfuric, hydrochloric, hydrobromic and nitric acids and in a mixture of hydrochloric acid and potassium pyrophosphate, 0.2 N to both, are plotted in Fig. 1. In each case there were present 260 mg. of the hydrous alumina (equal to 172 mg. of Al_2O_3) and 200 ml. of the aqueous acid solution. The striking differences in rates of solution are obviously neither a function of hydrogen ion activity nor of diffusibility or valence of the ions. The rate of dissolution in the hydrofluoric acid solution was too great to

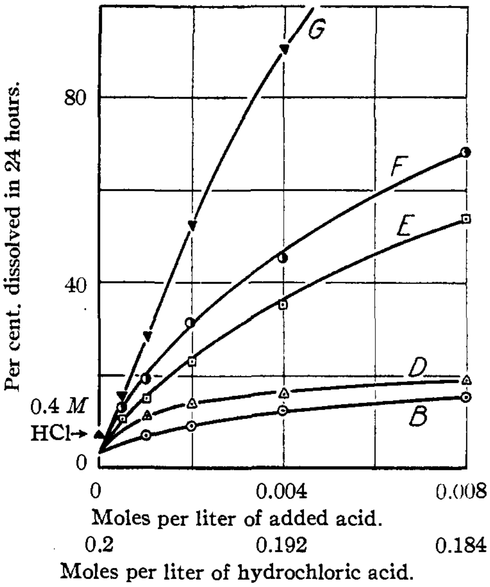

Fig. 2A.—The influence of the concentration of certain acids on the amount of the hydrous oxide (Specimen "A") dissolved in one day, 260 mg. of $Al_2O_3 \cdot 2.89H_2O$ was added to 200 ml. of solutions of HCl containing an added acid (B) H_2SO_4, (D) Oxalic, (E) H_3PO_4, (F) H_3PO_3, (G) H_2F_2. These suspensions were rotated at 25° for 24 hours, centrifuged, and the supernatant solutions analyzed for dissolved aluminum ion. The arrow indicates per cent. dissolved in 0.4 M HCl in 24 hours.

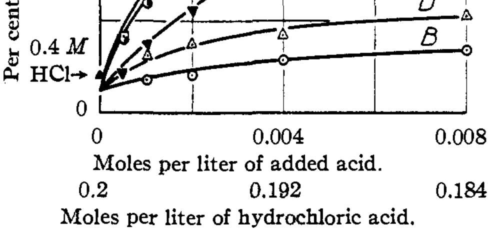

Fig. 2B.—The influence of the concentration of certain acids on the amount of hydrous oxide (Specimen "B") dissolved in one day. 260 mg. of $Al_2O_3 \cdot 2.70H_2O$ was added to 200 ml. of solutions of HCl containing an added acid (B) H_2SO_4, (D) oxalic, (E) H_3PO_4, (F) H_3PO_3. (G) H_2F_2. These suspensions were rotated at 25° for 24 hours, centrifuged, and the supernatant solutions analyzed for dissolved aluminum ion. The arrow indicates per cent. dissolved in 0.4 M HCl in 24 hours.

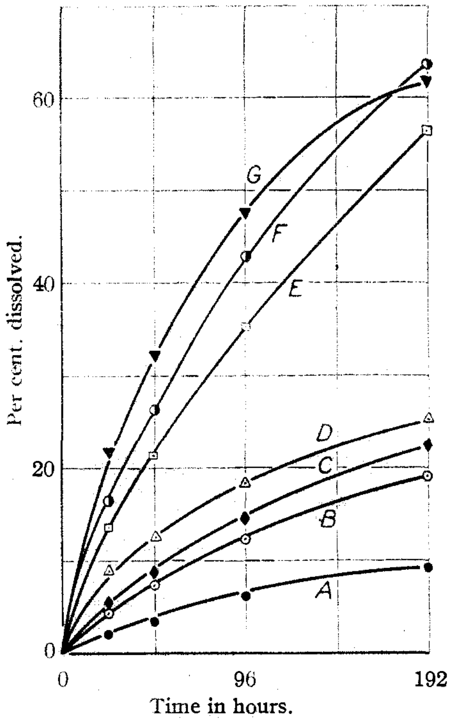

Fig. 3A.—The catalytic effect of anions on the rate of dissolution of the hydrous oxide (Specimen "A") in hydrochloric acid. 520 mg. of $Al_2O_3 \cdot 2.89H_2O$ was added to 200 ml. of 0.198 *M* HCl which was also 0.001 *M* (B) H_2SO_4, (D) Oxalic, (E) H_3PO_4, (F) H_3PO_3, (G) H_2F_2. Curve (A) represents the rate in 0.2 *M* HCl, and (C) the rate in 0.4 *M* HCl.

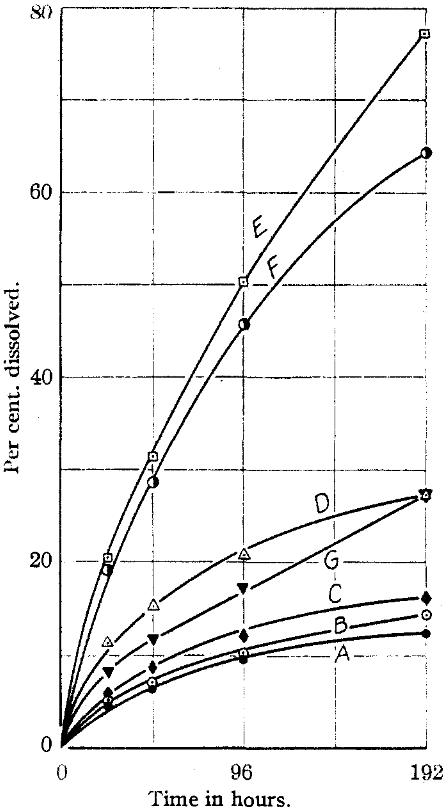

Fig. 3B.—The catalytic effect of anions on the rate of dissolution of hydrous oxide (Specimen "B") in hydrochloric acid. 520 mg. of $Al_2O_3 \cdot 2.70H_2O$ was added to 200 ml. of 0.198 *M* HCl which was also 0.001 *M* (B) H_2SO_4, (D) oxalic, (E) H_3PO_4, (F) H_3PO_3, (G) H_2F_2. Curve (A) represents rate in 0.2 *M* HCl. and (C) the rate in 0.4 *M* HCl.

plot in this figure, the oxide having completely dissolved to a clear crystalloidal solution in about six minutes. In 0.2 *N* hydrofluosilicic acid the solution was complete in about two hours. The measurements were always made in duplicate and sometimes in triplicate, showing a reproducibility to 3%.

In the next series of measurements, the results of which are given in Figs. 2A and 2B, the acid solutions, 200 cc. in each case, consisted of mixtures of hydrochloric acid, 0.2 to 0.184 *M* plus one of the other acids, 0.0 to 0.008 *M*. (For consistency we are using the molecular formula H_2F_2 to represent a mole of hydrofluoric acid.) In the case of Specimen "A," 260 mg. was taken, as in the first instance; the amount of Specimen "B" was also 260 mg. (equal to 176 mg. of Al_2O_3). The time of reaction was twenty-four hours. It is seen that small amounts of the added acids influence greatly the rate of dissolution. In the experiments with both oxide specimens, the effect of 0.4 *M* hydrochloric acid was measured also, the result shown by the arrow on the ordinate axis demonstrating that doubling the concentration of hydrochloric acid was less effective than substituting very small amounts of the diverse acids for part of the 0.2 *M* hydrochloric.

The data in Figs. 2A and 2B show clearly that the amount of oxide dissolved in twenty-four hours in an acid solution is dependent upon the nature and concentration of the anions present and upon the temperatures at which the oxides were prepared.

It is observed that while hydrofluoric, phosphorous, and phosphoric acids greatly accelerate the rate of solution of both oxide specimens, their order of effectiveness differs in the two cases. This change in order will be considered under "Discussion of Results." In passing it might be mentioned that the rates of dissolution of the natural modifications of calcium sulfate—alabaster, fibrous gypsum and selenite—in water have been shown to be different in each of the three cases.[8]

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[8] Wildermann, *Z. physik. Chem.*, **66**, 445 (1909).

A series of measurements upon the time of dissolution of the oxide specimens (520 mg.) in 200-cc. portions of solution mixtures, 0.198 *M* with respect to hydrochloric and 0.001 *M* with respect to other acids, again showed the striking influence of traces of certain anions. These results are plotted in Figs. 3A and 3B. With the exception of the added sulfuric acid, it is noted that the added anions increased the rate in 0.2 *N* solution more than was effected by doubling the concentration of hydrochloric acid.

In order to determine the influence of extent of surface of the oxide, experiments were performed in which 200-ml. portions of acid solutions, 0.198 *M* with respect to hydrochloric and 0.001 *M* with respect to other acids, were allowed to act for twenty-four hours upon various weights of the oxide specimens. Figures 4A and 4B summarize the results. The weight of oxide dissolved in unit time is a function of the weight of solid (surface exposed) present, and of the temperature at which the oxide was prepared. The effect of the anions in accelerating the rate of dissolution tends to reach a maximum. This is the usual type of phenomena encountered in heterogeneous reactions when the catalyst is exerting its maximum influence; a further increase in the surface has relatively no influence on the rate of the reaction. It will be noticed that the small concentration of hydrofluoric acid used is much less effective in catalyzing the dissolution of Specimen "B" than Specimen "A." This is a significant point which will be discussed later in connection with a consideration of the difference in the two types of hydrous oxides.

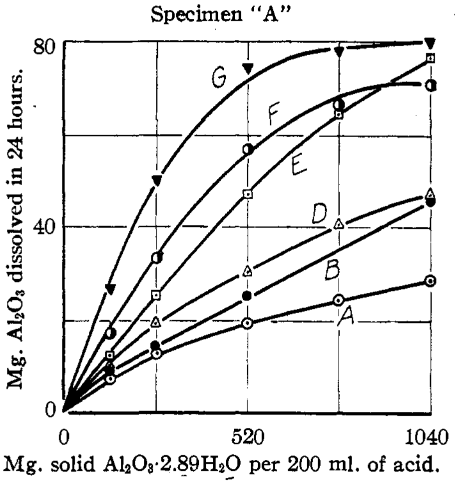

Fig. 4A.—The influence of surface area of hydrous alumina on amount dissolved. Different weights of $Al_2O_3 \cdot 2.89H_2O$ were added to 200 ml. of 0.198 *M* HCl which was also 0.001 *M* (A) H_2SO_4, (D) oxalic, (E) H_3PO_4, (F) H_3PO_3, (G) H_2F_2. Curve (B) represents the amount dissolved in 0.8 *M* HNO_3. The suspension was rotated for 24 hours at 25°, centrifuged, and the supernatant solutions analyzed for aluminum ion.

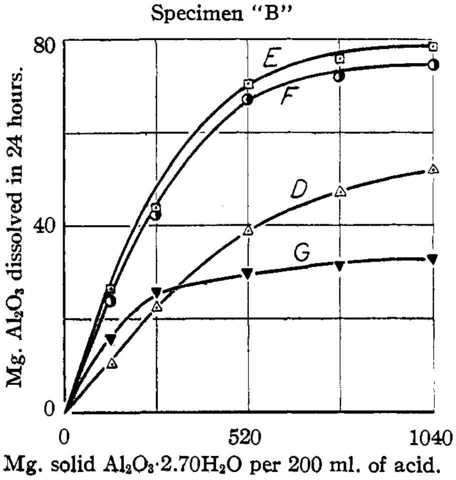

Fig. 4B.—The influence of surface area of hydrous alumina on amount dissolved. Different weights of $Al_2O_3 \cdot 2.70H_2O$ were added to 200 ml. of 0.198 *M* HCl which was also 0.001 *M* (D) oxalic, (E) H_3PO_4, (F) H_3PO_3, (G) H_2F_2. The suspensions were rotated at 25° for 24 hours, centrifuged, and the supernatant solutions analyzed for aluminum ion.

Discussion of Results

The explanation of these facts lies in the structural arrangement of the oxide and the specific nature of the anions, the formula $Al_2O_3 \cdot x(H_2O)$ not adequately representing the structure of the hydrous oxide.

Previous publications from this Laboratory have described the processes of olation and oxolation which take place when hydrous oxide hydrosols are aged at room temperature, which processes are accelerated upon heating.[9] These concepts are based on the Werner–Pfeiffer[10] ideas of hydrolysis and olation, together with Stiasny's[11] concept of oxolation. It is also agreed that oxolation may take place through a reaction of the type suggested originally by Küntzel, Riess and

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[9] (a) Thomas and Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) Thomas and Tai, THIS JOURNAL, **54**, 841 (1932); (c) Thomas and von Wicklen, *ibid.*, **56**, 794 (1934); (d) Thomas and Vartanian, *ibid.*, **57**, 4 (1935); (e) Thomas and Kremer, *ibid.*, **57**, 1821, 2538 (1935); (f) Thomas and Owens, *ibid.*, **57**, 1825, 2131 (1935); (g) Thomas and Miller, *ibid.*, **58**, 2526 (1936).

[10] (a) Pfeiffer, *Ber.*, **40**, 4036 (1907); (b) *Z. anorg. Chem.*, **56**, 275 (1907); (c) Werner, *Ber.*, **40**, 2113 (1907).

[11] (a) Stiasny and Balanyi, *Collegium*, 86 (1927); (b) Stiasny, "Gerbereichemie," Verlag von Theodor Steinkopff, Dresden-Blasewitz, Germany, 1931, p. 351.

Königsfeld.[12] The hydrous alumina specimens are polyolated, polyoxolated structures in which there are also hydroxo and aquo groups sufficient with the ol and oxo bridges to satisfy the coördination number of aluminum.

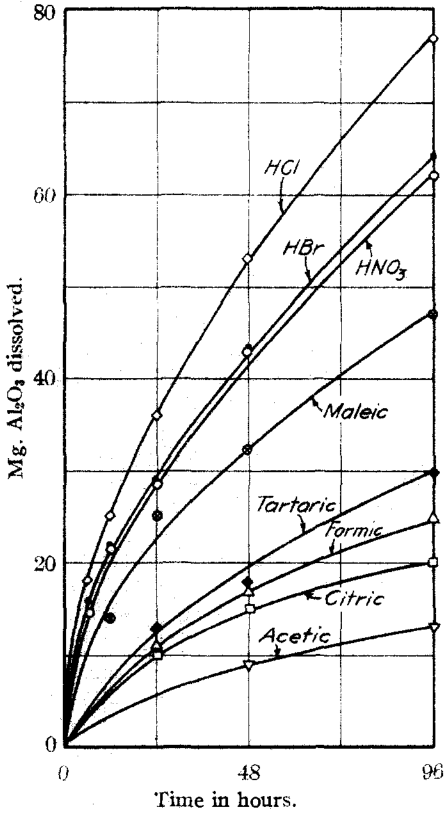

Fig. 5.—The dissolution of the hydrous oxide (Specimen "A") in diverse acids. 2.000 g. of $Al_2O_3 \cdot 2.89H_2O$ was added to 200 ml. of the 0.2 N acid solution, rotated at 25° for the desired time, a drop of $(NH_4)_2SO_4$ was added the solutions were then centrifuged and the supernatant solutions analyzed for dissolved aluminum ion.

For an acid to dissolve hydrous alumina and produce crystalloidal solutions of aluminum ions, it is necessary then that (1) the hydroxo groups be converted to aquo groups, (2) the ol bridges be broken and the hydroxo groups thus produced converted to aquo groups and (3) oxo bridges, if present, also be converted to hydroxo groups, etc. The first reaction is accomplished readily by oxonium ion, while (2) ol bridges are well known to be quite stable in the presence of oxonium ion and (3) oxo bridges are extremely resistant to attack by oxonium ion.

Since elevation in temperature favors the conversion of ol bridges to oxo bridges—*i. e.*, favors oxolation—one would expect Specimen "B," the hydrous oxide prepared by the action of boiling water upon aluminum amalgam, to be more oxolated than Specimen "A" which was prepared by the action of water at room temperature. Specimen "A" is perhaps predominantly an ol complex containing some oxo bridges and probably similar in structure to hydrargillite. Megaw[13] has submitted evidence for an olated structure for this mineral. Specimen "B" seems to be predominantly an oxo complex resulting from the partial oxolation of an olated structure possessing, to be sure, hydroxo groups as well as oxo bridges. This latter type, predominating in "B" and present to a minor extent in "A," may be the diaspore or chain-type structure referred to in recent literature.[14]

Considering now the dissolution of these hydrous oxides in aqueous acid solutions, it is apparent, since one of the products of the reaction is water, that the energy of formation of water furnishes the driving force for the reaction. But the potential energy of the ol $(\text{Al}\overset{\text{H}}{\text{O}}\text{Al})$ link in the solid phase, or the oxo $(\text{Al}\overset{\text{Al}}{\text{O}}\text{Al})$ link, is not readily available, as is evident from the slowness of the reaction of the solid hydrous oxide with the strong acids, hydrochloric, hydrobromic and nitric. Before an oxonium ion can react with an ol or oxo link it is necessary to form an intermediate link, the formation of which contributes toward the work required to break an ol or oxo link. Essentially this idea was suggested by London[15] for organic substitution reactions, and has been investigated by Polanyi,[16] Olsen[17] and Hammett.[18]

In other words, an intermediate complex must be formed, the formation of which renders the ol and oxo group reactive toward oxonium ion; and it is obvious that this intermediate complex involves anions, indeed, specific anions.

It is postulated in this paper that the formation of this complex is the rate-determining factor of the dissolution process.

Hydrargillite has been described[19] as an aluminum ion surrounded by six hydroxyl groups at the

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(12) Küntzel, Riess and Königsfeld, *Collegium*, 270 (1935).

(13) Megaw, *Z. Krist.*, **87**, 185 (1934).

(14) (a) Ewing, *J. Chem. Phys.*, **3**, 203 (1935); (b) Jander and Winkel, *Z. anorg. Chem.*, **200**, 257 (1931); (c) Fricke, *Kolloid Z.*, **69**, 312 (1934).

(15) London, *Z. Elektrochem.*, **35**, 552 (1929).

(16) (a) Meer and Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932); (b) Bergman, Polanyi and Szabo, *ibid.*, **B20**, 161 (1933).

(17) (a) Olsen, *J. Chem. Phys.*, **1**, 418 (1933); (b) Olsen and Voge, THIS JOURNAL, **56**, 1690 (1934).

(18) Roberts and Hammett, *ibid.*, **59**, 1063 (1937).

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

corners of a distorted octahedron, the oxygen atoms being polarized in such a manner as to have directed bonds at the corners of an irregular tetrahedron. Two of the bonds of a hydroxyl group go to aluminum ions, at a third the hydrogen is found, and the fourth represents a concentration of negative electricity which has directed toward it the hydrogen belonging to another hydroxyl group. In this manner the coördination numbers of six for aluminum, four for oxygen and two for hydrogen are satisfied. It is this kind of hydroxyl group that is postulated to be present in our hydrous oxide, Specimen "A," and which is referred to here as an ol group.

It is easy to understand then why an ol group should not react readily with a proton, the oxygen of the ol group being already attached to three positive ions.

When an anion which forms complexes with an aluminum ion in acid solution, such as fluoride, phosphate, phosphite, oxalate or sulfate, approaches the aluminum ion in an ol $(\mathrm{Al\overset{H}{O}Al})$ link at the surface, the bond between the aluminum approached and the oxygen will be broken. For convenience, we picture this in the following manner: $\mathrm{F^- \longrightarrow Al \ldots \overset{H}{O}Al}$. The ol group has now been converted into an hydroxo group which readily reacts[20] with a proton from an oxonium ion in the solution.

A similar mechanism would apply to the other anions, such as the $H_2PO_4^-$, $H_2PO_3^-$, $HC_2O_4^-$ and HSO_4^- ions or to their divalent anions.

It has been stated above that Specimen "B" is a more highly oxolated type of oxide than Specimen "A." By oxolation we mean that the proton of an ol group has migrated into a neighboring ol group, the result being an aquo group and an oxo group, with the simultaneous rearrangement of the structure to satisfy the coördination numbers of the atoms concerned. Such oxo groups exist in diaspore, according to Bernal and Megaw[19] and Ewing,[14a] the oxygen atom lying practically in the same plane with three coördinating aluminum ions[21] while the fourth coördination position is that of a weak hydroxyl bond of a neighboring hydroxyl group. Diaspore has the formula AlOHO.

If such oxo groups occur in Specimen "B" one might reasonably expect that an anion such as the $H_2PO_4^-$ ion would be a more effective catalyst than a F^- ion in dissolving Specimen "B." This idea follows from the fact that the $H_2PO_4^-$ ion is a proton donor as well as a coördinative binder, whereas the F^- ion is only a coördinative binder. Perhaps the (FHF^-) ion is the catalyst in breaking up oxo links. Palmer[22] reported that the rate of solution of quartz in hydrofluoric acid was proportional to the concentration of (FHF^-) ion rather than to the concentration of the hydrofluoric acid.

Davies[23] has shown that the (FHF^-) ion is present in aqueous hydrofluoric acid in much smaller amounts than is the F^- ion. If it is assumed that the (FHF^-) ion is the catalyst in breaking up an oxo group, one can account for the difference in the action of hydrofluoric acid on Specimens "A" and "B," this difference being due to the more limited chances of collision between the (FHF^-) ion than the F^- ion with the surface of the oxide.

Both Specimens "A" and "B" dissolve in maleic, tartaric, formic, citric and acetic acids at rates which are less than the rate of dissolution in nitric acid of the same equivalent concentration (Fig. 5). Therefore, since there is no correlation between the strength of the acid and the rate at which the hydrous oxides dissolve, the catalytic effect of certain anions cannot be explained on the basis of general acid-base catalysis. For example, the dissociation constants of phosphoric and maleic acids are very nearly the same, whereas the rates of dissolution of the hydrous oxides in these two acids are markedly different. Furthermore, while tartaric, hydrofluoric and formic acids are all approximately of the same strength, there is a great difference between hydrofluoric on the one hand and tartaric and formic on the other hand in their action upon the oxides.

The dissociation constants of oxalic and phosphorous acids are approximately the same. Figure 1 shows the great difference in the rapidity of dissolution of Specimen "A" in these two acids.

(20) Hydroxo groups also can be displayed by coördinative binding anions, as shown in this Laboratory by the unpublished results of Mr. P. D. Baker. *E. g.*, the *p*H of 200 cc. of an aqueous suspension containing 260 mg. of hydrous oxide specimens increased from *p*H 7 to 10.5 (Specimen "B") and to *p*H 9.6 (Specimen "A") when sufficient potassium fluoride was added to make the solution 0.1 *M* KF (the *p*H of pure aqueous 0.1 *M* KF was 7.2). The same weight of Specimen "A" also raised the *p*H of 200 cc. of 0.1 *M* solutions of the following salts: (a) $K_2C_2O_4$ from 7.1 to 8.4, (b) K_2SO_4 from 5 to 7.1, (c) KCl from 5.5 to 6.8, (d) KBr from 5.7 to 6.4, (e) KNO_3 from 5.7 to 6.3. Natural specimens of hydrargillite and of diaspore also react with a potassium fluoride solution in a similar manner.

(21) Previously the expression "oxo group" has been used in papers from this Laboratory to designate an oxygen ion coördinated between two metallic ions.[12,14] In this paper the idea of "oxo group" is modified to conform to the recent picture[14a] referred to.

(22) Palmer, *J. Chem. Soc.*, 1656 (1930).

(23) Davies and Huddleston, *ibid.*, **125**, 260 (1924).

While the equivalent conductivities of hydrofluosilicic acid and sulfuric acid are practically the same,[24] only two hours were required to dissolve completely 260 mg. of Specimen "A" in 200 ml. of 0.1 *M* hydrofluosilicic acid, whereas five hundred and fifty hours were required to dissolve 80% of the same weight of Specimen "A" in the same volume and concentration of sulfuric acid.

Neither can the catalytic effect of certain of these anions be ascribed to a "salt effect," since the ionic strength of all the aqueous acid solutions would be less than the ionic strength of sulfuric acid of the same equivalent concentration. Rates of dissolution of both Specimens "A" and "B" were investigated in sulfuric and hydrochloric acid solutions of the same calculated ionic strength, and it was found that the sulfuric acid dissolved the hydrous oxides more rapidly under these conditions than did the hydrochloric acid.

It is concluded that the effect of an anion on the rate of dissolution of hydrous aluminum oxide is a specific property of that anion and is not applicable to any generalization, other than that if the anion is a coördinative binder with the aluminum ion even small amounts of it will catalyze the dissolution of the oxide when added to other acids whose anions are not such strong coördinative binders or complex formers.

The mechanism offered above might be useful in explaining why phosphates and fluorides reduce the passivity of aluminum metal in nitric acid.[25]

Turning back to a further discussion of the relatively slow rate of dissolution of the hydrous oxides in citric and tartaric acids, it should be recalled that the anions of these acids form complexes with the aluminum ion in neutral or alkaline solutions. However, the complexes are supposedly of the chelate type, involving the α-hydroxy group of the anion. The dissociation of the proton of this α-hydroxy group would be exceedingly slight in acid solution. Therefore, one would not expect these acids to catalyze the dissolution of the hydrous oxide in acid solutions, since there could be very little complex formation at the solid–liquid interface.

There is another essential difference in the nature of the two hydrous oxide Specimens "A" and "B" which we have not discussed. This difference is as follows. When a gram of Specimen "B" is shaken for a moment with 200 ml. of 0.2 *M* nitric, hydrochloric or hydrobromic acid, about 90% of the oxide is dispersed to the colloidal state, *i. e.*, (1) it remains in suspension when centrifuged at 3000 r. p. m. for thirty minutes; (2) it passes readily through the pores of filter paper but does not pass through the pores of a nitrocellulose membrane; (3) it shows a pronounced Tyndall effect; and (4) it is readily precipitated by ammonium sulfate. Only about 5% of the same weight of Specimen "A" will be colloidally dispersed by the same acids under the same conditions.

To explain the facts just stated it is assumed that there are more hydroxo groups on the surface[26] of particles of Specimen "B" than of Specimen "A." The hydroxo groups react readily with oxonium ions, rendering the particles positively charged and dispersing these particles as colloidal micelles, which ultimately will be broken to the crystalloidal state.

Summary

Certain anions, *viz.*, fluoride, phosphate, phosphite, oxalate and sulfate, or their acids, greatly accelerate the rate of dissolution of hydrous aluminum oxide in 0.2 molar hydrochloric acid solution even when present at a concentration of 0.001 molar.

This phenomenon cannot be explained on the basis of increased acid strength, increased diffusibility of the acid, valence of the anion or general acid–base catalysis.

An explanation based on the coördination structure of the hydrous oxide and the formation of a complex at the solid–liquid interface has been offered.

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(24) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1925, Vol. VI, p. 942.

(25) (a) Tartar and Cone, THIS JOURNAL, **56**, 48 (1934); (b) Centnerszwer and Wittandt, *Z. Elektrochem.*, **35**, 582 (1929).

(26) The presence of hydroxo groups on the surface of the hydrous oxide (Specimen "B") can be demonstrated readily: Dissolve 1 mg. of dry phenolphthalein in 3 ml. of 1,4-dioxane and divide the solution equally in three separate test-tubes. To (1) add anhydrous sodium carbonate; if the solution contains no water it remains colorless. To (2) add a pellet of dry potassium hydroxide. A pink color appears immediately at the interface between the liquid and the solid. This color will remain indefinitely at the interface and will not diffuse into the solution. This is because of the insolubility of potassium hydroxide in the dioxane. To (3) add 0.1 g. of hydroxy aluminum oxide prepared as Specimen "B" was, and the interface will immediately become pink. This color can be removed by the introduction of carbon dioxide and does not reappear on standing. The addition of water does not restore the color; however, the addition of more solid oxide does cause the color to reappear.