Hydrolytic Behavior of Gallium(III) Perchlorate

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Solutions of gallium(III) perchlorate at different base-to-gallium ratios and equilibrated at 50 and 75° have been studied. The data, along with characterization of the solid phase as GaOOH, indicate that equilibrium can be represented by the equation $GaOOH(c) + 3H_{aq}^+ \rightleftarrows Ga_{aq}^{3+} + 2H_2O$. The polymerization of the gallium solute species during the lengthy periods leading up to equilibrium is found to be a function of the ionic strength, the base ratio, and the initial polymerization number. Such variable behavior does not affect the nature of the ultimate equilibrium species.

Introduction

Evidence for the formation of cationic polymers in aqueous solutions of gallium(III) perchlorate has been reported.[1,2] The average molecular weight changes as a function of time and a solid phase eventually precipitates. Such behavior immediately raises the question of the nature of these solutions at equilibrium, but since the publication of these results, no attempts to characterize the equilibrium state have been reported.

The present communication presents the results of the light-scattering technique to study the solute species of equilibrated solutions of gallium(III) perchlorate at varying $\bar{n} = OH:Ga^{3+}$. Aging was speeded up by heating. (On the basis of the time necessary to reach equilibrium at 50 and 75°, we estimate that at least 2 years would be required at 25°.) Turbidity variations with time prior to equilibrium were measured also for selected solutions. Temperature variations do not change the nature of the equilibrium gallium solute species although the concentrations are certainly affected.

Experimental Section

Solution Preparation.—Gallium(III) perchlorate was prepared from the metal and concentrated perchloric acid.[3] The product was dissolved in distilled water to give stock solutions of approximately the desired concentrations.

Stock sodium perchlorate solution was prepared from F. G. Smith crystals, recrystallized two times.

Sodium hydrogen carbonate solutions were prepared by weight using the Fisher salt and checked by analysis.

Baker and Adamson 70% perchloric acid and Fisher 50% sodium hydroxide were used to prepare standard acid and base solutions.

Solutions for study were prepared in 100-ml volumetric flasks by diluting an aliquot of the gallium stock with 20–40 ml of water, adding the amount of sodium hydrogen carbonate calculated to give the desired $\bar{n}$, and then adding sufficient sodium perchlorate to give a solution 1.00 M in this salt. Water was then added to the mark. The dropwise addition of base was made over 20–60 min from a calibrated buret. The solutions were stirred constantly during the addition to reduce high local concentrations of base. Each solution was measured for initial values of turbidity, refractive index gradient, and pH within 1 hr after preparation.

Solutions were also prepared from GaOOH (AIAG Metals, Inc.) by weighing the desired amount of solid and equilibrating with 1, 2, or 3 equiv of perchloric acid in 1 M NaClO₄.

The solutions were equilibrated in baths maintained within 0.1° of 50° and 75°. Water and water–Carbowax mixtures were used as bath liquids. Both Pyrex and polyethylene vessels were used with no apparent effect on the rate or nature of precipitation. Care was taken to ensure that the flasks were tightly closed and no water loss was detected. The solutions were placed in the baths immediately after the initial measurements were made.

Analyses.—Gallium in the stock solutions was determined as Ga₂O₃ and in equilibrium solutions by EDTA titration using Cu–PAN indicator.[4] Perchloric acid not removed in the preparation of the gallium perchlorate was determined by passing an aliquot of stock solution through a column of Dowex 50 in the acid form and calculating the original acid as the difference between the total titrated acid and that due to the gallium exchange.

Potassium acid phthalate was used as the primary standard for the standard base solutions.

Sodium hydrogen carbonate solutions were analyzed by adding an excess of standard acid to an aliquot of the solution, heating gently to remove the CO₂, and titrating the unreacted acid with standard base.

X-Ray Diffraction Patterns.—Solid samples from the solutions were compared using a General Electric XDR-5 X-ray diffractometer with Ni-filtered Cu Kα radiation. The samples were scanned between 15 and 45°, 2θ.

Densities and pH Measurements.—Densities were determined in a vacuum pycnometer at 25°. All pH values were determined at 25° with a Heath recording pH meter using a glass electrode and calomel reference. Both standard buffer solutions and standard acid in 1 M NaClO₄ were used to calibrate the system.

Light-Scattering and Refractive Index Measurements.—All measurements were made with light of wavelength 4358 Å. The differential refractive index measurements were made at 25° using a Phoenix differential refractometer. The assumption that these values hold for higher temperatures was found to be valid when checked at 50°, within the limits of experimental error.

The turbidity measurements and treatment of data have been described.[5] A Phoenix Model 2000 light-scattering photometer was used and the working standard for the instrument was used as the turbidity standard. The value for the working standard was checked by a trial determination of the molecular weight of raffinose. The photometer was fitted with a cored cell table which permitted circulation of liquid from a constant-temperature bath so that solutions could be thermostated in the scattering cells.

(1) T. Moeller and G. L. King, *J. Am. Chem. Soc.*, **74**, 1355 (1952).

(2) J. K. Ruff and S. Y. Tyree, *ibid.*, **80**, 5654 (1958).

(3) L. S. Foster, *Inorg. Syn.*, **2**, 26 (1946).

(4) I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry," Part II, Vol. 2, Interscience Publishers, New York, N. Y., 1962, pp 85–87.

(5) F. C. Hentz and S. Y. Tyree, *Inorg. Chem.*, **3**, 844 (1964).

Results and Discussion

Solutions at Equilibrium.—In these studies we have assumed equilibrium to be established when values of turbidity, pH, and gallium concentration remained constant over a 2–3 week period. The results of the light-scattering study on the equilibrium solutions are summarized in Table I. It is obvious that the average

TABLE I

POLYMERIZATION DATA FOR EQUILIBRIUM SOLUTIONS

[Ga^{3+}], M		Initial	Temp,	[NaClO$_4$],		
Initial	Final	$\bar{n}$	°C	M	z'	$N_{z'}$
0.050	0.037	0.5	50	1.00	2.5	1.03
0.050	0.029	1.0	50	1.00	3.0	0.97
0.050	0.013^6	2.0	50	1.00	2.5	1.00
0.058	0.013	2.0	50	0.15		1.0 (estd)
0.050	0.029^6	0.5	75	1.00	2.5	0.99
0.058	0.025^5	1.0	75	1.00	2.5	0.93
0.045	0.007	2.0	75	1.00	2.5	1.10
0.030	0.002	2.0	75	0.07		1.0 (estd)

degree of polymerization, $N_{z'}$, is very nearly 1 for a net ionic charge of $z' = 2.5$. The estimates for solutions in the absence of added supporting electrolyte are less certain and are based on the net turbidity over background compared with the other solutions. The time required to reach equilibrium varied. At 50° 2 or 3 months was necessary. At 75° this was reduced to 3–4 weeks.

The usual concentration *vs.* $1/N_{z'}$ plots could not be employed to determine the best charge since the final gallium(III) concentration range for a given $\bar{n}$ was not great enough to give meaningful plots. We have, therefore, chosen to present for each solution the data for the minimum charge that gives a polymerization number very nearly 1. The most common value for this charge is $z' = 2.5$ which means, of course, that any value less than 2.5 would give an unreasonable $N_{z'}$ of less than 1. It should be noted also that even for an assumed charge of 3.0 for the species, an $N_{z'}$ of 1.2–1.3 would be the maximum for each solution.

We conclude that monomeric Ga$_{aq}$$^{3+}$ ions are the predominant gallium solute species in the equilibrium solutions. Moreover, measurements on the solutions prepared from GaOOH(c) and H$^+$ showed similar results. If our conclusion is correct that the gallium species is Ga$_{aq}$$^{3+}$, the effective ionic charge, z', might be expected to be less than 3 owing to the high perchlorate concentration. This would mean that other hydrolysis products such as Ga(OH)$^{2+}$ are not present to any significant degree.

All solutions yielded a solid phase of fine white crystals which formed slowly over the equilibrium period. Initially these crystals adhered very tightly to the flask, but eventually they flaked off and dropped to the bottom of the flask as fine powder. This solid was washed thoroughly with water and dried for several hours at 100°. The X-ray diffraction patterns showed all samples to have the same structure and to be identical with that of GaOOH.[6] The maximum *d*-spacing
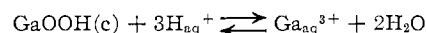
(6) "Powder Diffraction File," American Society for Testing and Materials, Philadelphia, Pa., 1967, No. 6-180.

difference was 0.06 Å for one peak, but generally the values were within 0.02 Å. The differences are probably due in part to errors in reading the recording since peak width and symmetry varied slightly among the samples. The over-all agreement was excellent.

The pH was measured primarily to determine if a change was occurring during the equilibrium period. The precision of the measurements is not high for two reasons: (1) the indicating electrode was sensitive to the high ionic strength of Na$^+$ClO$_4$$^-$ and (2) the equilibrium was established at one temperature and measurements were made at another.

In all cases the pH remained constant until the solid phase appeared. The hydrogen ion concentration increased slowly until precipitation ceased. Typical of the correspondence between the measured pH change and the calculated values based on the assumption that three hydroxide ions are removed by each gallium precipitated are the data from the second and seventh solutions in Table I. For the second solution the pH change from 2.20 to 1.75 indicated an increase in [H$^+$] of about 0.012 M compared to a calculated value of 0.013 M. In the seventh solution the value from the pH change (2.50 to 1.60) was about 0.024 M compared to 0.022 M. In general, for solutions with 1 M NaClO$_4$ supporting electrolyte, the final pH values fell within the range of 1.40–1.90 with the initial values measuring in the range 2.10–2.75 depending on the gallium concentration and $\bar{n}$. In the absence of the sodium perchlorate, the final values were slightly lower, corresponding to the decreased solubility of GaOOH.

As a result of the studies on the solution and solid phases, we feel the equilibrium is best represented as

$$\text{GaOOH(c)} + 3\text{H}_{aq}^+ \rightleftharpoons \text{Ga}_{aq}^{3+} + 2\text{H}_2\text{O}$$

for which the solubility constant expression is

$$\log K_s = \log [\text{Ga}^{3+}][\text{H}^+]^{-3}$$

The pH values and gallium concentrations have been used to calculate an approximate value for log K_s at the two temperatures. These values are listed in Table II. Our value in the ionic medium at 50° is in
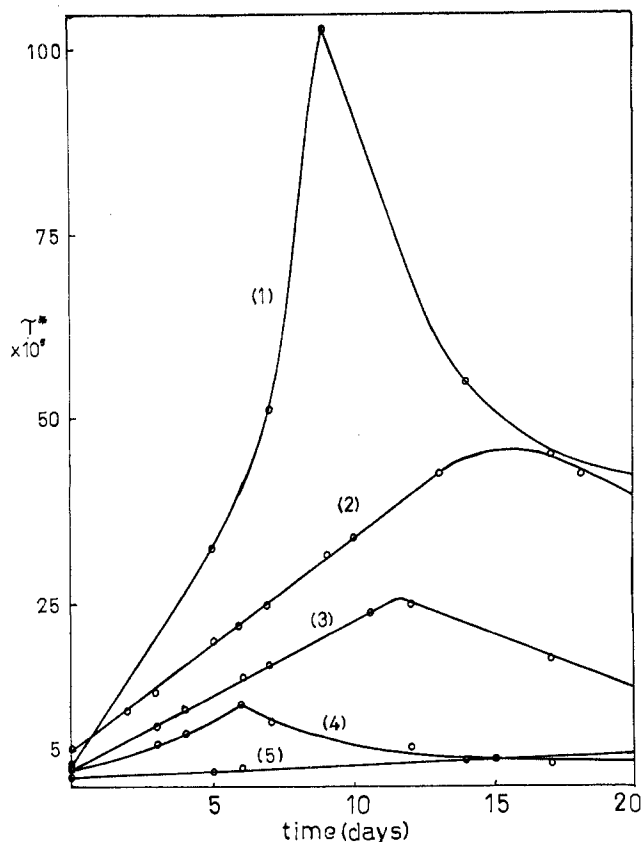
TABLE II

APPROXIMATE VALUES OF LOG K_s FOR EQUILIBRIUM SOLUTIONS

Temp, °C	1 M NaClO$_4$	No NaClO$_4$ added	3 M NaClO$_4$
50	3.7	3.2	
75	2.8		
75	2.8^a	2.2	
60			3.66^b

^{a} Prepared from GaOOH(c) and H$^+$. ^{b} P. Schindler, personal communication, 1967.

fair agreement with that of Schindler which was obtained from equilibrations of GaOOH and H$^+$ using high-precision measurements.

Solution Behavior Prior to Equilibrium.—Figure 1 shows the variation of net turbidity, τ^* (*i.e.*, that due to the gallium solute species), as a function of time for several solutions under different conditions of temperature, $\bar{n}$, concentration, and ionic strength. Data for
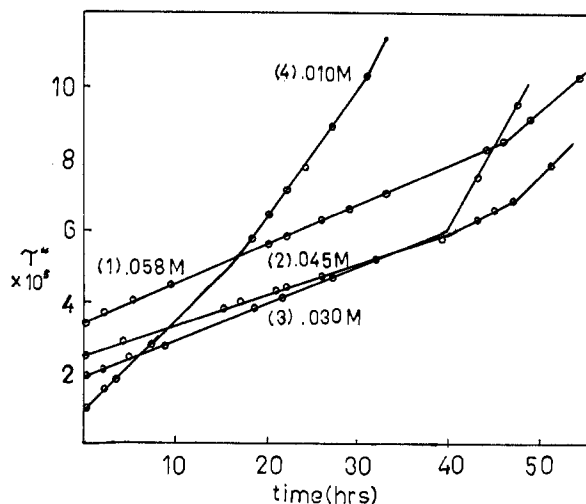
Figure 1.—Variation of τ^* with time for solutions in Table III.

Figure 2.—τ^* vs. time at 50° for solutions with $\bar{n} = 2.0$ and the indicated gallium concentration. Initial $N_{z'}$ values ($z' = 0$): (1) 6.1, (2) 5.2, (3) 6.8, (4) 10.0.

TABLE III

DATA FOR SOLUTIONS PRIOR TO EQUILIBRIUM[a]

Curve	[Ga³⁺], M	$\bar{n}$	$N_{z'}(z' = 0)$ Initial	Max
1	0.050	2.25	6.5	295
2	0.100	2.0	5.3	45
3	0.058	2.0	5.2	45
4[a]	0.058	2.0	5.3	20 (estd)
5	0.050	1.0	1.2	15

[a] The temperature was 50° for all experiments and [NaClO₄] = 1.00 M, except in expt 4 where [NaClO₄] = 0.15 M.

the curves, including minimum ($z = 0$) values of $N_{z'}$, are listed in Table III. The actual measurements were made at 25° and the solutions had to be removed from the temperature bath and filtered before each measurement once precipitation had started. At a given temperature, the rate of increase of τ^* seems to be primarily a function of $\bar{n}$ and secondarily dependent on the concentration. The effect of supporting electrolyte is seen clearly be comparing curves 3 and 4. A 25° curve for solution 4 showed a very slight initial increase and then a steady value over 5 months and never approached the higher values of curve 4. The majority of the data were taken on 50° equilibrations because the reactions could be followed most easily at this temperature.

For solutions with $\bar{n} \leq 2$ and 1 M NaClO₄, the turbidity increase is a straight-line function of time. Such linear behavior is a characteristic of condensation polymerization[7,8] and the rate of condensation should be a function of the initial monomer concentration.

In order to check this hypothesis and, hopefully, to determine a rate constant for the polymerization, a series of $\bar{n} = 2$ solutions of varying gallium concentration was prepared. Figure 2 shows the variation of τ^* with time for these solutions. The measurements were made with the scattering cell thermostated at 50° in the photometer. Consistent data were obtained until precipitation was indicated by the first change in slope. At this time solid could be seen to deposit on the cell faces.

It is immediately obvious that, although the linear relationship holds, the rate of increase is more dependent on the initial $N_{z'}$ than the concentration. We must conclude, therefore, that it is invalid to assume that a common "monomer" unit exists in all $\bar{n} = 2$ solutions and that the rate constant is unique for each solution. There are two possible reasons for this observation. First, the more dilute in gallium a solution is for a given $\bar{n}$, the less acidic it is. This would tend to increase the hydrolysis rate for the less acidic solutions. Second, one of the serious limitations in studying metal and metalate ionic polymerizations is the uncertainty of a reproducible initial state. The larger initial $N_{z'}$ values and more rapid polymerization of the solutions lower in gallium concentration may be a result of insufficiently well-controlled variables in solution preparation, whereby local high concentrations of base are not avoided entirely.

It should be noted that the high ionic strength affects not only the rate of polymerization and the maximum $N_{z'}$ but also the time necessary for precipitation to begin. For example, a solution identical with solution 4 in Figure 1 showed evidence of a solid phase after 1 month at 25° whereas a portion of solution 1 kept at 25° required over 2 months. For a solution 1 M in sodium perchlorate, with $\bar{n} = 2$, 4 months was necessary for precipitation at 25°, and with $\bar{n} = 1$, even the

(7) G. Oster, *J. Colloid Sci.*, **2**, 291 (1947).
(8) M. F. Bechtold, *J. Polymer Sci.*, **4**, 219 (1949).

turbidity had not changed after 6 months. The same relative behavior was observed at 50° where solution 4 precipitated in 5–8 hr. The reason for the earlier precipitation in the absence of excess electrolyte is probably related to the increased solubility of GaOOH in the ionic medium or to the competition between the polymerization and precipitation reactions.

Although the polymerization and variable behavior prior to equilibrium do not affect the nature of the final gallium species, the importance of the variables of time, temperature, and ionic strength in studies of polyionic systems is emphasized. A situation similar in several

respects to this one arises in the case of iron(III) solutions where variable polymerization behavior is observed, but wherein the equilibrium data can be interpreted in terms of the solid hydroxide and Fe^{3+} ions in solution.[9,10]

(9) W. Feitknecht and W. Michaelis, *Helv. Chim. Acta*, **45**, 212 (1962).
(10) P. Schindler, W. Michaelis, and W. Feitknecht, *ibid.*, **46**, 444 (1963).

Transfer Reactions Involving Boron.   XX.
Disproportionation Reactions of Alkyl-, Alkoxy-, and Haloboranes[1]

By D. J. PASTO,[2a] V. BALASUBRAMANIYAN, and P. W. WOJTKOWSKI[2b]
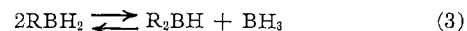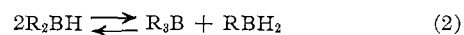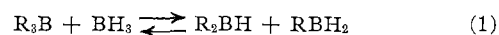
The solution redistribution equilibria of borane with alkylboranes, alkoxyboranes, haloboranes, and arylmercaptoboranes have been studied. The results obtained with the various systems are discussed individually and compared with each other and, when available, with gas-phase and other data appearing in the literature. The redistribution of trialkylboranes with borane in tetrahydrofuran produces a mixture of mono-, di-, and trialkylboranes and borane, the first two being the predominant products. Complicating the systems are the presence of five hydrogen-bridged monomer–dimer equilibria. The equilibrium constants for these equilibria have been determined for the *n*-propyl- and isopropylborane systems. The reaction of 1 or 2 mol of alcohols with 1 mol of borane produces dialkoxyboranes in kinetically controlled reactions. The dialkoxyboranes undergo slow redistribution reactions to give mixtures of borane and di- and trialkoxyboranes. Similarly, trialkyl borates and borane undergo slow disproportionation reactions. The redistribution equilibrium constants are identical, within experimental error, for primary and secondary alkoxyborane systems; however, the *t*-butoxyborane equilibrium constant is significantly different. The rate of attainment of equilibrium is markedly dependent on the structure of the alkoxy group. Boron trichloride reacts with borane to give either mono- or dichloroborane depending on the stoichiometry of the starting reagents, whereas boron trifluoride does not react with borane.

Borane–Trialkylboron Disproportionations

Schlesinger and coworkers[3,4] have observed that simple trialkylborons react with diborane, in the absence of solvent, to produce a complex equilibrium mixture of diborane and mono-, di-, tri-, and tetraalkyldiboranes. Brown and coworkers[5] have studied the disproportionation of tri-*n*-pentylboron with borane in tetrahydrofuran. They observed that the kinetically controlled (1 hr at 0°) product distribution formed in the hydroboration of 300 mmol of 1-pentene with 150 mmol of borane differs quite substantially (BH_3, 32.0%; RBH_2, 9.5%; R_2BH, 6.1%; R_3B, 52.4%) from the thermodynamically controlled product distribution

formed on allowing the reaction mixture to stand at room temperature (BH_3, 2.7%; RBH_2, 24.0%; R_2BH, 61.3%; R_3B, 12%).[6]

Our studies on the mechanism of the hydroboration reaction required a more careful analysis of the disproportionation reactions (eq 1–3) which could conceivably compete with the hydroboration reaction. The rate of the disproportionation of tri-*n*-propyl- and triisopropylboron with borane in tetrahydrofuran was followed by quenching aliquots of the reaction mixtures with *cis*-2-butene followed by glpc analysis of the resulting mixture of trialkyl-, dialkyl-*sec*-butyl-, alkyldi-

$$R_3B + BH_3 \rightleftarrows R_2BH + RBH_2 \qquad (1)$$

$$2R_2BH \rightleftarrows R_3B + RBH_2 \qquad (2)$$

$$2RBH_2 \rightleftarrows R_2BH + BH_3 \qquad (3)$$

(3) H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, **57**, 621 (1935).
(4) H. I. Schlesinger, L. Horvitz, and A. B. Burg, *ibid.*, **58**, 407 (1936).
(5) H. C. Brown, A. Tsukamoto, and D. B. Bigley, *ibid.*, **82**, 4703 (1960).