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Solutions of Gallium(I) Salts in Aqueous Base<sup>1</sup>

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The characteristic reaction of the so-called gallium dichloride with water has been known for a considerable time. With ample amounts of water a strongly reducing, flocculent, orange-brown to black precipitate is produced together with smaller amounts of hydrogen and gallium. The precipitate evolves hydrogen slowly on standing as the solid turns white or rapidly on addition of acids with ultimate solution of the product.<sup>2</sup> Although the identity of this precipitate has never been carefully studied, the supposition has been made that it is gallium(II) hydroxide produced by hydrolysis of the reactant  $\text{GaCl}_2$  since the empirical formula for the latter suggests a dipositive state.<sup>3</sup> However, subsequent, diverse studies have amply shown that the gallium dihalides are actually the gallium(I) salts  $\text{Ga}^+(\text{GaX}_4)^{4-6}$  and that the above reaction with water is characteristic of gallium(I) compounds since it occurs not only in the presence of the  $\text{GaX}_4^-$  anion but also with  $\text{AlCl}_4^-$ ,  $\text{AlBr}_4^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ .<sup>4, 7</sup>

Because of the strong reducing character of the gallium(I) oxidation state, very little information has been reported regarding its solution properties. Solutions of the above precipitate (or gallium(I) salts directly) in dilute acids exhibit little if any reducing strength once the system is clear of suspended particles; however, there have been reports

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of reducing solutions from the action of concentrated hydrochloric acid on the metal, where  $\text{Ga}^+$  may be strongly complexed.<sup>8,9</sup> Recently Schug and Sodowski<sup>10</sup> have presented stoichiometric evidence that hot, concentrated (11 M) perchloric acid reacts with metal to yield hydrogen plus the  $\text{Ga}^+$  intermediate and that this rapidly reduces the perchlorate ion, possibly because the latter is a kinetically more favorable homogeneous reaction in this solvent than production of hydrogen. Anodic oxidation of gallium in anhydrous acetic acid has been shown to yield a gallium solute with an average oxidation number between 1.25 and 2 that slowly evolves hydrogen from the solvent and reduces some of the stronger oxidizing agents.<sup>11,12</sup> A similar oxidation in liquid ammonia gives a relatively stable solution with the gallium in an average oxidation state of about 2.25.<sup>13</sup> In neither study was the presumed solution of gallium(I) further characterized. Although the unipositive state has been reported to have at best only a transient existence in aqueous solutions, it was observed some time ago that alkaline solutions of the dark precipitate described above or of a gallium(I) salt itself are actually surprisingly stable. Some characterization of the stability and reducing properties of this system are contained in the present paper.

Solution of a gallium(I) salt such as  $\text{Ga}_2\text{Cl}_4$  in aqueous NaOH gives, as with pure water, a black to dark orange precipitate, but this readily redissolves and the solution proceeds through shades of orange and yellow to colorless in a few tens of minutes. The initially vigorous reaction, probably largely due to the hydrolysis of the  $\text{GaCl}_4^-$  ion, produces some

5 to 25% (depending on sample size) of the total possible hydrogen by reduction of water and also 5 to 20% of the theoretical amount of metal through disproportionation (data for 2 M  $\text{OH}^-$ ). The production of metal may be responsible for the initially dark color of the precipitate; it should be emphasized that gallium metal is obtained only during the initial reaction with water. The resulting solution evolves hydrogen homogeneously and not from the walls of the glass container, so that the quiescent liquid becomes highly supersaturated ('pinpoint hydrogenation'). The kinetics of this reaction in 1 to 4 M NaOH have been measured by following the rate of hydrogen evolution from vigorously stirred solutions. The net reaction  $[\text{Ga}^+] + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Ga}(\text{OH})_4^- + \text{H}_2$  was found to be first order in gallium(I). Data taken from the time the solution process appeared complete, 5 to 10 min. after addition of base, were in agreement with those taken after the solution lost its light yellow to orange color 15 to 40 min. later, the longer time pertaining to solutions lower in hydroxide concentration. Rate constant results obtained for solutions initially 3.5 to 10 millimolar in gallium(I) are summarized in Table I.<sup>14</sup> Comparison of the rate constants for solvents maintained at a fixed, total concentration of 2 or 4 M by  $\text{NaClO}_4$  indicates that the reaction is also first order in hydroxide (0.95 to 1.0 observed) over the range studied. Gallium(III) was found to be without significant effect on the rate although at the 0.05 M level it virtually eliminates production of metal during the initial solution process. As an indication of the stability of these solutions, the rate constant in 1.00 M base corresponds to a half life of



Table 1

PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE DECOMPOSITION  
OF ALKALINE SOLUTIONS OF  $\text{Ga}(\text{GaCl}_4)$  AT 22-24°

NaOH M	added M	rate constant $\text{sec}^{-1} \times 10^5$
0.998	-----	$3.7_3 \pm 0.1$
1.99	-----	$8.3_7 \pm 0.2$
1.99	0.05 $\text{Ga}(\text{III})$	$8.2_1 \pm 0.1$
1.99	0.3 $\text{I}^-$	$8.5_4 \pm 0.1$
4.00	-----	$\sim 27 \pm 9$
0.990	1.00 $\text{NaClO}_4$	$4.17_7 \pm 0.04$
0.992	2.98 $\text{NaClO}_4$	$5.06 \pm 0.06$
1.986	2.00 $\text{NaClO}_4$	$9.9_3 \pm 0.3$
2.982	1.02 $\text{NaClO}_4$	$14.6 \pm 0.5$

5.2 hours. The increasing reactivity with increasing hydroxide concentration, contrary to that for a reaction involving proton reduction, suggests that the reaction effectively takes place through an interaction of  $\text{OH}^-$  with the solvated  $\text{Ga}^+$  ion to inductively affect transfer of the two 4s electrons to water of solvation, forming hydrogen either directly (and probably intramolecularly) or via a hydride intermediate. Attempts to detect hydrogen atoms or other intermediate, free radicals were substantially negative; emulsion polymerization of styrene in 0.05 M NaOH using Dreft as the emulsifying agent gave only faint amounts of turbidity with gallium(I) although a peroxydisulfate-sulfite mixture was found to initiate this system satisfactorily. In contrast to the behavior

in base, a solution of  $\text{Ga}_2\text{Cl}_4$  in 0.3 M  $\text{HClO}_4$  produced a negligible quantity of hydrogen after the 12 min. necessary to get the initial precipitate into solution, although an orange-brown color persisted for more than an hour.

Careful neutralization of the basic solutions provides the interesting result that all of the reduced gallium is reversibly precipitated as a flocculent, white precipitate resembling hydrous  $\text{Ga}_2\text{O}_3$ . The reduced gallium is relatively stable in this form and may be kept for more than a week stored under water. On slow addition of acid the solid begins to evolve hydrogen at about pH 5, and the solution is slow even at a pH of 1 to 2. In the latter case the system is free of reducing strength before the material has completely dissolved. The manner in which the reduced gallium is so precipitated is not known. No suggestion of an analogue of a gallium(I) gallate is found in the behavior of univalent ions such as  $\text{Ag}^+$ ,  $\text{Tl}^+$  or  $\text{Na}^+$ , as these are not precipitated along with hydrous  $\text{Ga}_2\text{O}_3$  under the same conditions. On the other hand it is possible that such a small  $d^{10}s^2$  ion as  $\text{Ga}^+$  could be truly amphoteric, although no success in fractionation of the two oxidation states at higher pH values was evidenced in preliminary experiments. Electromigration and ion exchange experiments and precipitation studies with solutions containing less than the equivalent amount of gallium(III) or other anions might be informative.

A considerable number of reducing reactions of the basic solutions of  $\text{Ga}_2\text{Cl}_4$  were investigated. Concentrated solutions were made up to be between 0.5 and 1 M in  $\text{Ga}^+$  and near 1 M in free base (presuming  $\text{Ga}(\text{OH})_4^-$  is formed from  $\text{GaCl}_4^-$ ) so that indications of the reduction potential would be more significant. In addition to reactions expected

with the stronger oxidizing agents, basic gallium(I) solutions readily reduce to the metallic element, unless otherwise noted, 1 M NaOH solutions of  $\text{Ti}^+$ ,  $\text{AsO}_2^-$ ,  $\text{Cd}(\text{CN})_2^{2-}$  (+ 1M  $\text{CN}^-$ ) and 1 M NaOH saturated with solid  $\text{PbO}$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{TlI}$ ,  $\text{CdS}$ ,  $\text{SnO}_2$  and, with warming,  $\text{Fe}_2\text{O}_3$  (to  $\text{Fe}_3\text{O}_4$ ) and  $\text{Zn}(\text{OH})_2$ . Reaction is not found with solutions of  $\text{CrO}_2^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{SeO}_3^{2-}$ , as well as  $\text{ClO}_4^-$  and  $\text{SO}_4^{2-}$ ; kinetic limitations alone are apparently responsible for the lack of reaction with all of these but  $\text{CrO}_2^-$  (vide infra). From the standard reduction potential for  $\text{Zn}(\text{OH})_2$ -Zn,<sup>8</sup> the weakest couple for which reaction is observed, an  $E_B^\circ$  value of 1.24 v. or greater is estimated for  $[\text{Ga}^+] + 4\text{OH}^- = \text{Ga}(\text{OH})_4^- + 2e^-$ . With 1.29 v. for  $\text{Ga-Ga}(\text{OH})_4^-$ ,<sup>15</sup> the Ga-Ga(I) potential is 1.39 v. or less.

The fleeting existence of  $\text{Ga}^+$  in acid makes any estimate of the potential for the  $\text{Ga}^+ - \text{Ga}^{3+}$  couple therein somewhat more difficult. Reactions of a variety of oxidizing agents with  $\text{Ga}^+$  in acid were tested by addition of the neutral reagent to the reducing precipitate at pH 5-7 followed by slow acidification. The majority of the observed reactions occurred at the point where the precipitate began to dissolve and release hydrogen rapidly, i. e., at a pH of 0 to 2. Reduction of stronger oxidizing agents under these conditions include  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ ,  $\text{SeO}_3^{2-}$  to Se and the kinetically more difficult  $\text{SeO}_4^{2-}$  to Se and  $\text{ClO}_4^-$  to  $\text{Cl}^-$ . The element was also obtained from solutions of  $\text{Sn}^{2+}$ ,  $\text{As(III)}$ ,  $\text{Cd}^{2+}$  and from solid  $\text{PbCl}_2$ , while  $\text{SO}_3^{2-}$  was reduced to  $\text{H}_2\text{S}$  and Se effectively to  $\text{H}_2\text{Se}$  as a further product from the above selenates. No reaction under these conditions was found with the solids  $\text{PbSO}_4$ ,  $\text{TlCl}$ ,  $\text{TlI}$  and solutions of  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and (probably)  $\text{Cr}^{3+}$ . Although uncertainties as the effective



pH and the state of the product gallium(III) may diminish somewhat the quantitative significance of these observations, reduction of  $\text{Cd}^{2+}$  occurs at a sufficiently high acidity that its standard potential allows a like, lower limit of approximately 0.40 v. to be assigned to  $\text{Ga}^+ - \text{Ga}^{3+}$ . With the known  $E^\circ$  value for  $\text{Ga} - \text{Ga}^{3+}$ ,<sup>8</sup> an approximate maximum of 0.79 v. can then be established for  $\text{Ga} - \text{Ga}^+$ .

It will be noted that there is a significant difference between the (maximum) values so estimated for the  $\text{Ga} - \text{Ga(I)}$  couple in acid and in base, 0.79 and 1.39 v. respectively. Although the acid value is probably less reliable, the  $\text{Ga}^+ - \text{Ga}^{3+}$  potential estimated directly would have to be 0.10 v., in distinct conflict with the observed reduction of  $\text{Cd}^{2+}$ , in order for the above, derived values to agree. A more plausible explanation would be that the  $\text{Ga} - \text{Ga}^+$  couple is indeed not pH independent, as expected for the simple hydrated ion, but rather that gallium(I) is more stable in base by about 0.6 v. due to a specific complexing reaction with the hydroxide ion. Such a condition might also be inferred from the enhanced kinetic stability of such a solution as well as the precipitation behavior discussed earlier.

Taken at face value, the above estimated potentials indicate that gallium(I) should be stable with respect to disproportionation in either acid or base. However, this conclusion may appear somewhat equivocal when it is noted that the minimum potentials deduced for  $\text{Ga(I)} - \text{Ga(III)}$  would have to be only 0.13 and 0.05 v. larger, respectively, in order to have an equilibrium constant of unity for the disproportionation. That

such an over-all decomposition reaction is not observed other than during the initial, vigorous solution process has already been noted. Although the atomically dispersed metal so produced could conceivably react as rapidly as formed with the acidic or basic solutions at the concentrations used, contrary to the behavior of the bulk metal, it is difficult to see how a rate-determining disproportionation reaction in base could be first order in gallium(I). The effect of gallium(III) in almost eliminating the formation of metal during the initial solution process may, however, be the result of a reaction with the finely dispersed metal.

As noted above, a definite reduction of  $\text{ClO}_4^-$  to  $\text{Cl}^-$  is obtained as the precipitate goes into solution in dilute  $\text{HClO}_4$  although the yield is small compared to the evolution of hydrogen. The perchlorate ion is, of course, both a much weaker and a notoriously slower oxidizing agent under such conditions than in the hot, concentrated acid where this reaction is also indicated,<sup>10</sup> so that further evidence of the reducing capabilities of Ga(I) is provided. A considerable reduction of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (to S and  $\text{H}_2\text{S}$ ) is also observed on direct solution of  $\text{Ga}_2\text{Cl}_4$  in the 0.1 N acids.

Other, more direct methods for the production of the basic gallium(I) solutions have also been investigated. The equilibration of a solution 2 M in NaOH and 0.05 M in Ga(III) with liquid gallium metal for 24 hours does not give any detectable amount of reducing strength in solution, presumably due to kinetic limitations according to the above data. Similarly, the common method for production of metal, the reduction of basic gallate solutions on a platinum cathode, gives no reducing intermediate in



either 1 or 3 M  $\text{OH}^-$ . However, the anodic oxidation of liquid gallium into well-stirred 1 M NaOH (at 35° and 17 to at least 170 ma./cm.<sup>2</sup>) does produce definite amounts of gallium(I), although the (undetermined) efficiency for this does not appear to be particularly large.<sup>16, 17</sup> Concentration of the reducing strength after such anodic oxidation by precipitation of the mixed oxide thereby allows the preparation of moderately concentrated solutions far more easily than via a gallium(I) salt. The foregoing results, although to some extent preliminary in nature, do indicate some of the interesting and potentially useful properties of basic solutions of gallium(I).

### Experimental

The kinetics of reduction of  $\text{H}_2\text{O}$  by basic solutions of  $\text{Ga}_2\text{Cl}_4$  were studied in a sample container constructed from a 40/50 standard taper joint sealed at both ends to make a cell about 6 1/2 in. high. The internal stirrer consisted of a glass rod with a glass-enclosed, Alnico rod magnet sealed across the rod near the top and glass stirring blades fused onto the same rod near the bottom. The rod was bluntly pointed at both ends so that it fit into a dimple in the top of the container and the narrow opening of a capillary stopcock in the center of the bottom piece. The length of the stirrer was adjusted so that it could be turned rapidly with a minimum of vibration when the contacts were lubricated with a small amount of fluorocarbon grease. A conventional, magnetic stirrer inverted over the top of the cell actuated the stirring rod.

The sample of  $\text{Ga}_2\text{Cl}_4$ , prepared as before,<sup>4</sup> was introduced into the cell in the dry box or quickly in the atmosphere, the cell evacuated, and about 90 ml. of solvent admitted through the lower stopcock. The cell

was pressurized through an upper, side stopcock with  $N_2$  previously equilibrated with the solvent, and then opened to the gas buret. Hydrogen evolution was measured at constant pressure to  $\pm 0.01$  ml. for one to four half-lives, with the results corrected for the vapor pressure of the solution and for any changes in ambient pressure or temperature. The cell was also immersed in a large beaker of water and the stirrer air-cooled to reduce solution temperature variation during a run to less than  $1^\circ$ . The reducing strength at the completion of an experiment,  $C_t$ , was determined by addition of standard triiodide solution to an aliquot, followed by acidification and back titration. Atmospheric oxygen does not appear to show a significant reaction with the solutions. Most of the rate data were evaluated from the usual relationship between  $\log C$  and time, although the data were evaluated independently of  $C_t$  in the few cases where this value was uncertain from plots of the graphically derived function  $dC/dt$  vs.  $C$ . Commercial  $NaClO_4$  was found to contain impurities, probably  $NaClO_3$ , that react with iodine solutions, so that the data given in Table I were obtained using  $NaClO_4$  prepared by reaction of reagent grade  $NaOH$  and  $HClO_4$ . The  $NaClO_4$  and free acid or base concentrations in the product were determined by titration before and after exchange of the solution with Dowex-50 in the acid cycle.

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- (13). A. D. McElroy, J. Kleinberg, and A. W. Davidson, ibid., 74, 736 (1952).
- (14). There appears to be a decrease in rate after several half-lives at the highest base concentration although this was not investigated further.



- (15). Calculated from data given in "Stability Constants", compiled by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, Part II, Chemical Society, London, 1958, p. 21. The  $E_B^\circ$  of ca. 1.22 v. given by Latimer (Ref. 8) appears to be low since the acid ionization constant ( $K_{s4}^*$ ) estimated for the hydrous oxide  $[\text{Ga}(\text{OH})_3(\text{s}) + \text{H}_2\text{O} = \text{Ga}(\text{OH})_4^- + \text{H}^+]$  is only 0.25% of that given for the better characterized ionization of hydrous aluminum oxide, whereas the gallium compound is well recognized to be more acidic. A like value of  $E_B^\circ$ ,  $1.29 \pm 0.02$  v., is also obtained if  $\text{p}K_{sp}$  is taken as -35.0 to -36.5 ("Stability Constants") and  $\text{p}K_{s4}^*$  is assumed to be 1 to 2 units more positive than that given by Latimer for aluminum.
- (16). As expected, anodic oxidation of aluminum under these conditions gives no reducing, solute species.
- (17). Accordingly, studies of the dissolution of gallium in alkaline solution (J. O'M. Bockris and M. Enyo, J. Electrochem. Soc., 109, 48 (1962)) should include consideration of such a reaction.

**END**