

trast in reactivity serves to emphasize the ability of the complex to reduce only the more electrophilic carbonyl groups in polyfunctional compounds, hence this reagent seems to have great potential in organic synthesis.

We are actively examining other selective reductions as well as the further characterization of lithium *N*-dihydropyridylaluminum hydride,⁵ which may be isolated as a pale yellow crystalline solid from concentrated pyridine solutions.

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(6) It is especially desirable to ascertain whether I possesses a 1,2- or a 1,4-dihydropyridine moiety.

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EVIDENCE FOR Ga(I) AS AN INTERMEDIATE IN THE REACTION OF GALLIUM METAL WITH AQUEOUS PERCHLORIC ACID

Sir:

Evidence recently has been obtained for the existence of Ga(I) in the gallium dihalides¹ and in certain addition compounds of the gallium dihalides,² as well as in the anodic oxidation of gallium in glacial acetic acid.³ There appears to be no published evidence, however, for the existence of Ga(I) in aqueous solutions,⁴ although reference has been made to the persistence of reducing properties following the dissolution of gallium metal in aqueous hydrochloric acid.⁵

We wish to report certain observations on the stoichiometry of the reaction of gallium metal with perchloric acid which provides strong evidence for the participation of Ga(I) as an intermediate species in the reaction. The pertinent experimental observations are that in the reaction of the metal with hot 11 *M* (72 wt. %) perchloric acid each mole of Ga(III) produced is accompanied by the formation of *one-half* mole of H₂ and *one-fourth* mole of Cl⁻ ion.⁶ No other reduction products are formed in significant amount, in conflict with the implication by Foster that chlorine and other products are formed.⁷ The results from a typical experiment are tabulated

Gallium metal used	3.10 mmoles (0.2164 g.)
Hydrogen gas produced	1.55 mmoles (34.8 ml. S.T.P.)
Chloride produced	0.78 mmole
Cl ⁻ /Ga ratio	0.248
H ₂ /Ga ratio	0.50

The observed stoichiometry can be accounted for quantitatively by the mechanism

(1) R. K. McMullan and J. D. Corbett, *J. Am. Chem. Soc.*, **80**, 4761 (1958).

(2) S. M. Ali, F. M. Brewer, J. Chadwick and G. Garton, *J. Inorg. and Nuclear Chem.*, **9**, 124 (1959).

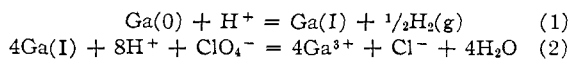
(3) A. W. Davidson and F. Jirik, *J. Am. Chem. Soc.*, **72**, 1700 (1950).

(4) The second edition of Latimer's "Oxidation Potentials," 1952, for example, discusses aqueous gallium chemistry in terms of the +2 and +3 oxidation states.

(5) L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

(6) The original observation concerning the Cl⁻-Ga(III) proportion was made in the course of some work recently carried out in collaboration with L. I. Katzin at the Argonne National Laboratory.

(7) L. S. Foster, "Inorganic Syntheses," Vol. II, 1946, p. 26.



The proposed mechanism involves highly selective behavior of Ga(0) and Ga(I) with respect to oxidation; the metal reacting predominantly with H⁺ rather than ClO₄⁻ or the intermediate chlorine compounds which must be involved in step two of the above mechanism, and the Ga(I) reacting predominantly with ClO₄⁻ rather than H⁺ despite the fact that H⁺ is certainly a sufficiently strong oxidizing agent to convert it to the trivalent state. On the basis of the present interpretation, gallium(I) joins the rather small group of ions which is capable of reducing perchlorate ion in aqueous solution.⁸ The reluctance of Ga(I) to reduce H⁺ provides an explanation for the slow rate of dissolution of the metal in the halogen acids as compared with HClO₄ and for the observed reducing properties of the solution after the metal is completely dissolved.

(8) W. R. King and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

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CRYSTALLINE POLYMERS OF THE 2,3-EPOXYBUTANES—STRUCTURE AND MECHANISM ASPECTS

Sir:

It was suggested previously,^{1,2} based on indirect evidence,³ that the stereoregular polymerization of propylene oxide to high molecular weight isotactic polymer occurs by a front-side displacement at its asymmetric carbon atom. We recently polymerized the *trans*- and *cis*-2,3-epoxybutanes to high yields of different crystalline high polymers.⁴ We now have evidence, based on polymerizing D(+)-2,3-epoxybutane to optically inactive crystalline polymer, which indicates that the stereoregular polymerization of *trans*-2,3-epoxybutane occurs by a rearward displacement on either of its equivalent asymmetric carbon atoms.

D(+)-2,3-epoxybutane, prepared by the procedure of Lucas and Garner,^{5,6} ($[\alpha]_D^{25} + 58.8^\circ$, lit.⁵ $+ 59.0^\circ$) was polymerized (1.0 g.) with an *i*-Bu₃Al-0.5 water catalyst⁷ (0.4 millimole Al) in *n*-heptane (6.1 g.) for 2 hr. at -78° . This polymerization, which was almost instantaneous, gave a 97% conversion to highly crystalline, heptane-insoluble polymer $[(\ln \eta_{rel})/C] 1.0$ (0.1%, CHCl₃, 25°), m.p. 96°] which was essentially optically inactive

(1) M. Osgan and C. C. Price, *J. Polymer Sci.*, **34**, 153 (1959).

(2) E. J. Corey, *Tetrahedron Letters*, **2**, 1 (1959).

(3) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).

(4) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 489 (1960).

(5) H. J. Lucas and H. K. Garner, *J. Am. Chem. Soc.*, **70**, 992 (1948).

(6) The starting D(-)-2,3-butanediol was kindly supplied (98% purity based on rotation) by Dr. R. W. Jackson and Dr. R. F. Anderson, U. S. D. A., Northern Utilization Research and Development Division, Peoria, Illinois. The final D(+)-2,3-epoxybutane was, by gas chromatography, 96.7% *trans*-2,3-epoxybutane, 0.5% *cis*-2,3-epoxybutane and 3.2% diethyl ether (ether added to remove water by azeotropic distillation).

(7) E. J. Vandenberg, *J. Polymer Sci.*, **47**, 486 (1960).