# Articles

## Reduction of Representative Organic Functional Groups with Gallane-Trimethylamine

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The rates and stoichiometry of the reaction of gallane-trimethylamine with selected organic compounds containing representative functional groups were examined in tetrahydrofuran solution under standardized conditions (THF, 0 °C). And its reducing characteristics were compared with those of aluminum hydride-triethylamine(AHTEA). The rate of hydrogen evolution from active hydrogen compounds varied considerably with the nature of the functional group and the structure of the hydrocarbon moiety. Alcohols, phenol, amines, thiols evolved hydrogen rapidly and quantitatively. Aldehydes and ketones were reduced moderately to the corresponding alcohols. Cinnamaldehyde was reduced to cinnamyl alcohol, which means that the conjugated double bond was not attacked by gallane-trimethylamine. Carboxylic acids, esters, and lactones were stable to the reagent under standard conditions. Acid chlorides also were rapidly reduced to the corresponding alcohols. Epoxides and halides were inert to the reagent. Caproamide and nitrile were stable to the reagent, whereas benzamide was rapidly reduced to benzylamine. Nitropropane, nitrobenzene and azoxybenzene were stable to the reagent, whereas azobenzene was reduced to 1,2-diphenylhydrazine. Oximes and pyridine N-oxide were reduced rapidly. Di-*n*-butyl disulfide and dimethyl sulfoxide were reduced only slowly, but diphenyl disulfide was reduced rapidly. Finally, sulfones and sulfonic acids were inert to the reagent under the reaction.

### Introduction

In 1939, H. C. Brown used diborane for the reduction of organic compounds containing a carbonyl group, which was the first application of boron hydrides for the reduction of organic functional groups.[1] The discovery of lithium aluminum hydride[2] and lithium borohydride[3] brought about a revolutionary change in the procedures utilized for the reduction of functional groups in organic chemistry. Of these two reagents, lithium borohydride[4] is a relatively mild reducing agent, practically specific to the carbonyl group in aldehydes, ketones, and esters. On the other hand, lithium aluminum hydride[5] is an exceedingly powerful reagent that attacks almost all reducible groups. Therefore, it has been studied for so many reducing agents to control the reducing abilities.[6-28] But, the previous studies were restricted to aluminium hydride and borohydride species.

In 1947, Lithium gallium hydride is synthesized and reported by Finholt, Bond, Schlesinger.[2] And in 1977, Schrink and Schriver reported modified method of synthesis of lithium gallium hydride in good yields and purification.[29] Recently we reported that reducing power of lithium gallium hydride showed generally more powerful than borohydride, but less than aluminium hydride.[30] On the other hand, the reducing characters of gallane, which is a Lewis acidic type hydride, has not been studied. It has been reported gallane itself is unstable, although gallane-trimethylamine complex is stable.[31,32] We therefore decided to examine the reducing characteristics of gallane-trimethylamine complex systematically toward the standard organic functionalities under standardized conditions (THF, 0 °C). And we also compared the reducing properties of this reagent to those of the aluminum hydridetriethylamine (AHTEA).[28]

### Results and Discussion

Gallane-trimethylamine was prepared by the reaction of lithium gallium hydride with trimethylammonium chloride in diethyl ether as reported by Shrink and Shriver.[31,32]

$$LiGaH_4+[(CH_3)_3NH]Cl \xrightarrow{(C_2H_5)O} GaH_3\cdot N(CH_3)_3+LiCl+H_2$$

The general procedure for reduction was to add 1 mmol of the organic compound to 1 mmol of gallane-trimethylamine in THF to give 8 mL of solution at 0 °C. The hydrogen evolved on adding the compound to the reagent was noted. After the desired reaction time, the solution was hydrolyzed and the hydrogen evolved was noted. The hydride utilized for reduction by the compound was calculated from hydrogen evolution. In this way, it was possible to arrive at a value for the number of hydrides utilized for the reduction.

In some cases the hydride-to-compound ratio of 4 : 1 was inadequate to achieve complete reduction. In such cases the hydride concentration was maintained constant, but the concentration of compound reduced to give a higher ratio.

**Reaction of Alcohols, Phenol, Amines, and Thiols.** The alcohols, phenol, and thiols examined all liberated hydrogen instantly and quantitatively. On the other hand, *n*-hexylamine and diethyl amine liberated only 1

**Table 1.** Reaction of Gallane-Trimethylamine with Representative Alcohols in Tetrahydrofuran at 0 °C

| Compound | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| 1-Hexanol | 0.5 | 0.99 | 1.00 | 0.01 |
| | 1.0 | 0.99 | 1.01 | 0.02 |
| | 3.0 | 0.99 | 1.00 | 0.01 |
| Benzyl alcohol | 0.5 | 0.99 | 0.99 | 0.00 |
| | 1.0 | 0.99 | 1.02 | 0.03 |
| | 3.0 | 0.99 | 1.00 | 0.01 |
| 3-Hexanol | 0.5 | 1.02 | 1.03 | 0.01 |
| | 1.0 | 1.02 | 1.04 | 0.02 |
| | 3.0 | 1.02 | 1.04 | 0.02 |
| 3-Ethyl-3-pentanol | 0.5 | 0.85 | 0.87 | 0.02 |
| | 1.0 | 0.91 | 0.94 | 0.03 |
| | 3.0 | 0.97 | 0.99 | 0.02 |
| | 6.0 | 1.01 | 1.02 | 0.01 |
| Phenol | 0.5 | 0.95 | 0.98 | 0.03 |
| | 1.0 | 0.98 | 1.01 | 0.03 |
| | 3.0 | 0.98 | 0.99 | 0.01 |

[a] 1 M of compound to 1.33 mmol of $GaH_3 \cdot NMe_3$ (4 mmol of hydride) in 8 mL of solution 0.125 M in compound and 0.5 M in hydride. [b] M of compound. cHydrogen evolved from blank minus the hydrogen evolved on hydrolysis of the reaction mixture after the indicated reaction period.

**Table 2.** Reaction of Gallane-Trimethylamine with Other Active Hydrogen Compounds in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| *n*-Hexylamine | 0.5 | 0.53 | 0.55 | 0.02 |
| | 1.0 | 0.69 | 0.70 | 0.01 |
| | 3.0 | 0.88 | 0.90 | 0.02 |
| | 6.0 | 1.01 | 1.02 | 0.01 |
| | 12.0 | 1.03 | 1.05 | 0.02 |
| Diethylamine | 0.5 | 0.85 | 0.87 | 0.02 |
| | 1.0 | 0.94 | 0.95 | 0.01 |
| | 3.0 | 0.99 | 1.01 | 0.02 |
| | 6.0 | 1.02 | 1.03 | 0.01 |
| | 12.0 | 1.03 | 1.05 | 0.02 |
| 1-Hexanethiol | 0.5 | 0.95 | 0.98 | 0.03 |
| | 1.0 | 0.95 | 0.96 | 0.01 |
| | 3.0 | 0.95 | 0.96 | 0.01 |
| Benzenethiol | 0.5 | 1.05 | 1.05 | 0.00 |
| | 1.0 | 1.05 | 1.06 | 0.01 |
| | 3.0 | 1.05 | 1.06 | 0.01 |

[a-c] See corresponding footnotes in Table 1.

equiv of hydrogen, and no more hydrogen evolution was observed for 24 h. The results are summarized in Tables 1 and 2.

In the reaction with a quantitative amount of aluminium hydride-triethylamine (AHTEA) complex, all of the alcohols, phenol and thiols examined liberate hydrogen instantly and quantitatively at room temperature. However, it reacted with *n*-hexylamine liberated 1 equiv was evolved relatively slowly to be complete in 3 h at room temperature.[28]

**Reduction of Aldehydes and Ketones.** All the aldehydes and ketones examined consumed one equivalent of hydride, indicating a moderate reduction rate to the corresponding alcohols. Cinnamaldehyde consumed one equiv of hydride to give a 89% yield of cinnamoyl alcohol estimated by GLC. No trace of hydrocinnamyl alcohol was detected by GLC examination of the product. This suggests

**Table 3.** Reaction of Trimethylamine-Gallane with Representative Aldehydes in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Caproaldehyde | 0.5 | 0.00 | 0.64 | 0.64 |
| | 1.0 | 0.00 | 0.92 | 0.92 |
| | 3.0 | 0.00 | 1.02 | 1.02 |
| | 6.0 | 0.00 | 1.02 | 1.02 |
| Benzaldehyde | 0.5 | 0.03 | 0.60 | 0.57 |
| | 1.0 | 0.03 | 0.89 | 0.86 |
| | 3.0 | 0.03 | 1.02 | 0.99 |
| | 6.0 | 0.03 | 1.02 | 0.99 |
| Cinnamaldehyde | 0.5 | 0.03 | 0.91 | 0.88 |
| | 1.0 | 0.05 | 1.08 | 1.03 |
| | 3.0 | 0.05 | 1.08 | 1.03 |
| | 24.0 | 0.05 | 1.12 | 1.07 |

[a-c] See corresponding footnotes in Table 1.

**Table 4.** Reaction of Gallane-Trimethylamine with Representative Ketones in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| 2-Heptanone | 0.5 | 0.04 | 0.51 | 0.47 |
| | 1.0 | 0.04 | 0.88 | 0.84 |
| | 3.0 | 0.04 | 1.01 | 0.97 |
| | 6.0 | 0.04 | 1.02 | 0.98 |
| Norcamphor | 0.5 | 0.03 | 0.76 | 0.73 |
| | 1.0 | 0.03 | 0.87 | 0.84 |
| | 3.0 | 0.03 | 1.03 | 1.00 |
| | 6.0 | 0.03 | 1.03 | 1.00 |
| Acetophenone | 0.5 | 0.02 | 0.67 | 0.65 |
| | 1.0 | 0.02 | 0.86 | 0.83 |
| | 3.0 | 0.02 | 1.03 | 1.01 |
| | 6.0 | 0.02 | 1.03 | 1.01 |
| Benzophenone | 0.5 | 0.02 | 0.74 | 0.72 |
| | 1.0 | 0.02 | 0.89 | 0.87 |
| | 3.0 | 0.02 | 1.03 | 1.01 |
| | 6.0 | 0.02 | 1.05 | 1.03 |
| Cyclohexanone | 0.5 | 0.02 | 1.03 | 1.01 |
| | 1.0 | 0.02 | 1.04 | 1.02 |
| | 3.0 | 0.02 | 1.04 | 1.02 |
| Methyl vinyl ketone | 0.5 | 0.06 | 0.87 | 0.81 |
| | 1.0 | 0.06 | 0.98 | 0.92 |
| | 3.0 | 0.06 | 1.05 | 0.99 |
| | 6.0 | 0.06 | 1.05 | 0.99 |
| 2-Cyclohexene-1-one | 0.5 | 0.02 | 0.42 | 0.40 |
| | 1.0 | 0.02 | 0.75 | 0.73 |
| | 3.0 | 0.02 | 0.93 | 0.91 |
| | 6.0 | 0.02 | 1.06 | 1.04 |
| | 12.0 | 0.02 | 1.07 | 1.05 |

[a-c] See corresponding footnotes in Table 1.

that double bond did not react with gallane-trimethylamine. The results are summarized in Tables 3 and 4.

On the other hand, in the reactions with AHTEA, all of the aldehydes and ketones examined reduced to the corresponding alcohols with a quantitative amount of hydride 0.5 h at room temperature. In the case of cinnamaldehyde, the reagent providing α,β-unsaturated alcohol in 97% yield.

**Reduction of Quinones.** The reduction of a quinone to a hydroquinone should utilize 2 equiv of hydride, one for reduction and the other for hydrogen evolution. On the other hand, the reduction of the quinone to the 1,4-dihydroxycyclohexadiene stage should require 2 equiv of hydride for reduction, without hydrogen evolution. On this basis, the stoichiometry in Table 5 showed the reduction of *p*-benzoquinone proceeded to give only 1,4-dihydroxycyclohexadiene. Anthraquinone also appeared to be reduced cleanly to 9,10-dihydro-9,10-anthracenediol within 3 h.

However, the reaction of *p*-benzoquinone with AHTEA slowly utilized 2 equiv of hydride per mol of compound of which 35% of hydride was used for hydrogen evolution and the remaining 65% for reduction, whereas anthraquinone consumed 2 equiv of hydride, of which 25% was for hydrogen evolution and 75% for reduction.[28]

**Reduction of Carboxylic Aicds and Derivatives.** Caproic and benzoic acids evolved instantly 1 equiv of hydrogen but reduction was not proceeded. Acetic or succinic anhydrides reacted with gallane-trimethylamine at a slow rate, showing only 2.81 and 1.94 hydride uptake respectively in 96 h. Acid chlorides rapidly reduced to the corresponding alcohols. The results are summarized in Table 6 and 7.

**Table 5.** Reaction of Gallane-Trimethylamine with Representative Quinones in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| *p*-Benzoquinone | 0.5 | 0.12 | 1.32 | 1.20 |
| | 1.0 | 0.12 | 1.70 | 1.58 |
| | 3.0 | 0.12 | 1.83 | 1.71 |
| | 6.0 | 0.12 | 2.02 | 1.90 |
| | 12.0 | 0.12 | 2.11 | 1.99 |
| Anthraquinone[d] | 0.5 | 0.13 | 1.86 | 1.73 |
| | 1.0 | 0.13 | 2.10 | 1.97 |
| | 3.0 | 0.13 | 2.15 | 2.02 |

[a-c] See corresponding footnotes in Table 1. dCompounds were added as solids.

**Table 6.** Reaction of Gallane-Trimethylamine with Representative Carboxylic Acids in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Caproic Acid | 0.5 | 0.97 | 1.00 | 0.03 |
| | 1.0 | 1.03 | 1.06 | 0.03 |
| | 3.0 | 1.03 | 1.07 | 0.04 |
| | 12.0 | 1.03 | 1.07 | 0.04 |
| Benzoic acid | 0.5 | 0.93 | 0.95 | 0.02 |
| | 1.0 | 0.98 | 1.01 | 0.03 |
| | 3.0 | 0.98 | 1.01 | 0.03 |

[a-c] See corresponding footnotes in Table 1.

**Table 7.** Reaction of Gallane-Trimethylamine with Representative Acyl Derivatives in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Acetic anhydrided | 0.5 | 0.03 | 1.67 | 1.64 |
| | 1.0 | 0.05 | 2.02 | 1.97 |
| | 3.0 | 0.05 | 2.03 | 1.98 |
| | 24.0 | 0.05 | 2.45 | 2.45 |
| | 48.0 | 0.05 | 2.84 | 2.79 |
| | 96.0 | 0.05 | 2.86 | 2.81 |
| Succinic anhydride[d] | 0.5 | 0.00 | 0.47 | 0.47 |
| | 1.0 | 0.00 | 0.74 | 0.74 |
| | 6.0 | 0.00 | 1.15 | 1.15 |
| | 48.0 | 0.00 | 1.96 | 1.96 |
| | 96.0 | 0.00 | 1.94 | 1.94 |
| Phthalic anhydride | 0.5 | 0.07 | 0.50 | 0.43 |
| | 1.0 | 0.09 | 0.59 | 0.50 |
| | 3.0 | 0.09 | 0.71 | 0.62 |
| | 24.0 | 0.09 | 1.16 | 1.07 |
| | 72.0 | 0.09 | 1.98 | 1.89 |
| Caproyl chloride | 0.5 | 0.03 | 1.73 | 1.70 |
| | 1.0 | 0.03 | 1.96 | 1.93 |
| | 3.0 | 0.03 | 2.05 | 2.02 |
| Benzoyl chloride | 0.5 | 0.03 | 1.89 | 1.86 |
| | 1.0 | 0.03 | 2.02 | 1.99 |
| | 3.0 | 0.03 | 2.08 | 2.05 |

[a-c] See corresponding footnotes in Table 1. [d] hydride/compound=6.

**Table 8.** Reaction of Gallane-Trimethylamine with Esters and Lactones in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Ethyl caproate | 0.5 | 0.03 | 0.06 | 0.03 |
| | 1.0 | 0.05 | 0.09 | 0.04 |
| | 3.0 | 0.05 | 0.09 | 0.04 |
| | 6.0 | 0.05 | 0.09 | 0.04 |
| Ethyl benzoate | 0.5 | 0.02 | 0.04 | 0.02 |
| | 1.0 | 0.04 | 0.07 | 0.03 |
| | 3.0 | 0.04 | 0.07 | 0.03 |
| | 6.0 | 0.04 | 0.08 | 0.04 |
| γ-Butyrolactone | 0.5 | 0.01 | 0.02 | 0.01 |
| | 1.0 | 0.01 | 0.02 | 0.01 |
| | 3.0 | 0.01 | 0.02 | 0.01 |
| | 6.0 | 0.01 | 0.02 | 0.01 |
| γ-Valerolactone | 0.5 | 0.02 | 0.03 | 0.01 |
| | 1.0 | 0.02 | 0.05 | 0.03 |
| | 3.0 | 0.02 | 0.06 | 0.04 |
| | 6.0 | 0.02 | 0.06 | 0.04 |
| Phthalide | 0.5 | 0.03 | 1.51 | 1.48 |
| | 1.0 | 0.03 | 2.00 | 1.97 |
| | 3.0 | 0.03 | 2.05 | 2.02 |
| | 6.0 | 0.03 | 2.05 | 2.02 |
| Isopropenyl acetate | 0.5 | 0.06 | 0.09 | 0.03 |
| | 1.0 | 0.08 | 0.11 | 0.03 |
| | 3.0 | 0.11 | 0.13 | 0.02 |
| | 6.0 | 0.11 | 0.13 | 0.02 |
| | 12.0 | 0.11 | 0.13 | 0.02 |

[a-c] See corresponding footnotes in Table 1.

**Table 9.** Reaction of Gallane-Trimethylamine with Representative Alkyl Halides in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Octyl bromide | 0.5 | 0.01 | 0.03 | 0.02 |
| | 1.0 | 0.03 | 0.05 | 0.02 |
| | 3.0 | 0.04 | 0.07 | 0.03 |
| | 6.0 | 0.04 | 0.07 | 0.03 |
| Octyl chloride | 0.5 | 0.03 | 0.04 | 0.01 |
| | 1.0 | 0.04 | 0.06 | 0.02 |
| | 3.0 | 0.04 | 0.07 | 0.03 |
| | 6.0 | 0.04 | 0.06 | 0.02 |
| Octyl iodide | 0.5 | 0.02 | 0.05 | 0.03 |
| | 1.0 | 0.03 | 0.07 | 0.04 |
| | 3.0 | 0.03 | 0.06 | 0.03 |
| | 6.0 | 0.03 | 0.07 | 0.04 |
| Benzyl chloride | 0.5 | 0.03 | 0.05 | 0.02 |
| | 1.0 | 0.03 | 0.05 | 0.02 |
| | 3.0 | 0.03 | 0.06 | 0.03 |
| | 6.0 | 0.03 | 0.06 | 0.03 |
| | 12.0 | 0.03 | 0.06 | 0.03 |

[a-c] See corresponding footnotes in Table 1.

On the other hand, the reaction of AHTEA with acids, the acids were reduced readily to the corresponding alcohols after immediate evolution of 1 equiv of hydrogen. Acid anhydrides also underwent quantitative reduction to the corresponding diols. Acid chlorides were reduced rapidly and cleanly to the corresponding alcohols.[28]

**Reduction of Esters and Lactones.** Most of the esters and lactones examined were inert to the gallane-trimethylamine under the standard conditions. Isopropenyl acetate was also stable to the reagent. This suggests that double bond did not react with this reagent. Phthalide consumed 2 equiv of hydride. The results are summarized in Table 8.

However, AHTEA reduced esters, lactones and acetates rapidly to the corresponding alcohols.[28]

**Reduction of Alkyl Halides.** All of the alkyl halides examined were stable to the reagent. The results are summarized in Table 9.

**Reduction of Epoxides.** All the epoxide examined did not react with gallane-trimethylamine. The results are summarized in Table 10.

The reaction of aliphatic epoxides with AHTEA gives the $S_N2$-type of ring-opened products exclusively, whereas the reaction of styrene oxide, an aromatic one, proceeds to afford a mixture of 77% 1-phenylethanol and 23% 2-phenylethanol.[28]

**Reduction of Amides and Nitriles.** Most of the amides and nitriles examined were inert to the reagent. However benzamide consumed 2 equiv of hydride slowly to give the corresponding amine. The results are summarized in Table 11.

However, AHTEA reduced amides and nitriles to all the corresponding amines.[28]

**Reduction of Nitro Compounds and Their Derivatives.** 1-Nitropropane, nitro- benzene and azoxybenzene were stable to the reagent. Azobenzene consumed 2 equiv of hydride for reduction in 12 h. The results are summarized in Table 12.

In the case of reaction of AHTEA with 1-nitropropane, 1-nitropropane readily consumed a total of 5 equiv for hydride with 2.5 equiv of hydride being utilized for hydrogen evolution and 2.5 equiv for reduction, corresponding to the 1,2-dialkylhydrizine stage. Nitrobenzene was also reduced to hydrazobenzene, but only slowly. Similarly, the reaction of azobenzene and azoxybenzene with a theoretical amount of the reagent proceeded very slowly.[28]

**Reduction of Other Nitrogen Compounds.** Cy-

**Table 10.** Reaction of Gallane-Trimethylamine with Representative Epoxides in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| 1,2-Butyrene oxide | 0.5 | 0.03 | 0.05 | 0.02 |
| | 1.0 | 0.03 | 0.06 | 0.03 |
| | 3.0 | 0.03 | 0.06 | 0.03 |
| | 6.0 | 0.03 | 0.07 | 0.04 |
| Styrene oxide | 0.5 | 0.02 | 0.05 | 0.03 |
| | 1.0 | 0.02 | 0.06 | 0.04 |
| | 3.0 | 0.02 | 0.06 | 0.04 |
| | 6.0 | 0.02 | 0.06 | 0.04 |
| Cyclohexene oxide | 0.5 | 0.01 | 0.04 | 0.03 |
| | 1.0 | 0.02 | 0.04 | 0.02 |
| | 3.0 | 0.02 | 0.04 | 0.02 |
| | 6.0 | 0.02 | 0.05 | 0.03 |

[a-c] See corresponding footnotes in Table 1.

**Table 11.** Reaction of Gallane-Trimethylamine with Representative Amides and Nitriles in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Caproamide | 0.5 | 0.24 | 0.26 | 0.02 |
| | 1.0 | 0.32 | 0.35 | 0.02 |
| | 3.0 | 0.46 | 0.49 | 0.03 |
| | 6.0 | 0.49 | 0.53 | 0.04 |
| | 12.0 | 0.52 | 0.56 | 0.04 |
| | 24.0 | 0.52 | 0.57 | 0.05 |
| Benzamide | 0.5 | 0.16 | 0.67 | 0.51 |
| | 1.0 | 0.23 | 1.02 | 0.79 |
| | 3.0 | 0.25 | 1.56 | 1.31 |
| | 6.0 | 0.30 | 1.83 | 1.53 |
| | 12.0 | 0.30 | 2.05 | 1.75 |
| | 24.0 | 0.30 | 2.29 | 1.99 |
| N,N-Dimethyl-benzamide | 0.5 | 0.02 | 0.03 | 0.01 |
| | 1.0 | 0.02 | 0.03 | 0.01 |
| | 3.0 | 0.02 | 0.03 | 0.01 |
| Capronitrile | 0.5 | 0.12 | 0.14 | 0.02 |
| | 1.0 | 0.14 | 0.15 | 0.01 |
| | 3.0 | 0.14 | 0.18 | 0.04 |
| | 6.0 | 0.14 | 0.19 | 0.05 |
| Benzonitrile | 0.5 | 0.11 | 0.13 | 0.02 |
| | 1.0 | 0.12 | 0.14 | 0.02 |
| | 3.0 | 0.12 | 0.14 | 0.02 |
| | 6.0 | 0.12 | 0.14 | 0.02 |

[a-c] See corresponding footnotes in Table 1.

**Table 12.** Reaction of Gallane-Trimethylamine with Nitro Compounds and Their Derivatives in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Nitropropane | 0.5 | 0.02 | 0.03 | 0.01 |
| | 1.0 | 0.02 | 0.04 | 0.02 |
| | 3.0 | 0.02 | 0.05 | 0.03 |
| | 6.0 | 0.02 | 0.07 | 0.05 |
| | 24.0 | 0.02 | 0.08 | 0.06 |
| Nitrobenzene | 0.5 | 0.06 | 0.08 | 0.02 |
| | 1.0 | 0.03 | 0.06 | 0.03 |
| | 3.0 | 0.03 | 0.06 | 0.03 |
| | 6.0 | 0.03 | 0.07 | 0.04 |
| | 24.0 | 0.03 | 0.07 | 0.04 |
| Azobenzene | 0.5 | 0.07 | 1.41 | 1.34 |
| | 1.0 | 0.07 | 1.48 | 1.41 |
| | 3.0 | 0.07 | 1.60 | 1.53 |
| | 6.0 | 0.07 | 1.82 | 1.75 |
| | 12.0 | 0.07 | 2.13 | 2.06 |
| Azoxybenzene | 0.5 | 0.03 | 0.06 | 0.03 |
| | 1.0 | 0.06 | 0.14 | 0.08 |
| | 3.0 | 0.06 | 0.13 | 0.07 |

[a-c] See corresponding footnotes in Table 1.

**Table 13.** Reaction of Gallane-Trimethylamine with Other Nitrogen Compounds in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Cyclohexanone oxime | 0.5 | 0.61 | 1.54 | 0.93 |
| | 1.0 | 0.85 | 1.90 | 1.05 |
| | 3.0 | 0.97 | 2.06 | 1.09 |
| | 6.0 | 1.00 | 2.16 | 1.16 |
| | 12.0 | 1.00 | 2.23 | 1.23 |
| | 24.0 | 1.00 | 2.36 | 1.36 |
| Phenyl isocyanate | 0.5 | 0.02 | 1.03 | 1.01 |
| | 1.0 | 0.02 | 1.05 | 1.03 |
| | 3.0 | 0.04 | 1.07 | 1.03 |
| | 6.0 | 0.05 | 1.06 | 1.01 |
| Pyridine | 0.5 | 0.02 | 1.03 | 1.01 |
| | 1.0 | 0.02 | 1.02 | 1.00 |
| | 3.0 | 0.03 | 1.03 | 1.00 |
| | 6.0 | 0.03 | 1.04 | 1.01 |
| Pyridine N-oxide | 0.5 | 0.02 | 1.51 | 1.49 |
| | 1.0 | 0.02 | 2.06 | 2.04 |
| | 3.0 | 0.02 | 2.46 | 2.44 |
| | 6.0 | 0.02 | 2.74 | 2.72 |
| | 12.0 | 0.02 | 2.99 | 2.97 |

[a-c] See corresponding footnotes in Table 1.

clohexanone oxime evolved 1 equiv of hydrogen at a moderate rate, and reduction proceeded slowly. Phenyl isocyanate and pyridine consumed 1 equiv of hydride rapidly. Pyridine N-oxide reduced completely in 12 h. The results are summarized in Table 13.

In the case of AHTEA, cyclohexanone oxime and phenyl isocyanate were reduced to the corresponding amines in 3 h. Pyridine consumed 2.04 equiv hydride for reduction in 48 h.[28]

**Reduction of Sulfur Compounds.** Diphenyl disulfide was rapidly reduced in 30 min, with 1 equiv of hydrogen. On the other hand, dibutyl disulfide was reduced quite slowly, requiring approximately 24 h for complete reduction. Dimethyl sulfoxide was reduced relatively slowly. Diphenyl sulfone, methanesulfonic acid and *p*-Toluenesulfonic acid monohydrate were inert to the reagent. The results are summarized in Table 14.

**Table 14.** Reaction of Gallane-Trimethylamine with Representative Sulfur Derivatives in Tetrahydrofuran at 0 °C

| Compound[a] | Time (hr) | Hydrogen evolved[b,c] | Hydride used[b,c] | Hydride used for reduction[b,c] |
|---|---|---|---|---|
| Di-*n*-butyl disulfide | 0.5 | 0.38 | 0.73 | 0.35 |
| | 1.0 | 0.38 | 1.01 | 0.63 |
| | 3.0 | 0.38 | 1.21 | 0.83 |
| | 6.0 | 0.38 | 1.25 | 0.92 |
| | 24.0 | 0.38 | 1.40 | 1.02 |
| Diphenyl disulfide | 0.5 | 0.78 | 1.81 | 0.99 |
| | 1.0 | 0.85 | 1.87 | 1.02 |
| | 3.0 | 0.97 | 1.99 | 1.02 |
| | 6.0 | 1.01 | 2.02 | 1.01 |
| | 24.0 | 1.01 | 2.03 | 1.02 |
| Dimethyl sulfoxide | 0.5 | 0.14 | 0.74 | 0.60 |
| | 1.0 | 0.16 | 0.89 | 0.73 |
| | 3.0 | 0.19 | 1.05 | 0.86 |
| | 6.0 | 0.23 | 1.22 | 0.99 |
| | 24.0 | 0.25 | 1.25 | 1.00 |
| Diphenyl sulfone | 0.5 | 0.02 | 0.04 | 0.02 |
| | 1.0 | 0.02 | 0.05 | 0.03 |
| | 3.0 | 0.02 | 0.05 | 0.03 |
| Methanesulfonic acid | 0.5 | 1.04 | 1.05 | 0.01 |
| | 1.0 | 1.04 | 1.05 | 0.01 |
| | 3.0 | 1.04 | 1.06 | 0.02 |
| *p*-Toluenesulfonic acid monohydrate | 0.5 | 2.98 | 3.00 | 0.02 |
| | 1.0 | 2.98 | 3.02 | 0.04 |
| | 3.0 | 2.98 | 3.01 | 0.03 |

[a-c] See corresponding footnotes in Table 1.

And, similar results obtained from AHTEA.[28]

## Conclusion

A systematic study of the reduction of representative organic compounds with gallane-trimethylamine in tetrahydrofuran at 0 °C has been complete. The results reveal that the reducing properties of gallane-trimethylamine is quite different from those of AHTEA, as the followings: Gallane-trimethylamine does not reduce carboxylic acids, esters, lactones, epoxides, nitriles, nitro compounds and azoxybenzene, whereas AHTEA reduce them. Gallane-trimethylamine reacts with disulfide and sulfoxide very slowly, AHTEA reactsc ompletely in 0.5 h. And Reduction of acid anhydride with gallane-trimethylamine proceeded quite slowly, whereas the reduction with AHTEA reduced that in 6 h. The comparison of reducing characteristics between gallane-trimethylamine and AHTEA is showned in Table 15.

Gallane-trimethylamine is a useful reagent for selective reduction when aldehydes ketones and acyl halides were mixed with carboxylic acids, esters, lactones, epoxides halides, nitriles, nitro compounds, azoxybenzene.

**Table 15.** Comparison of Reducing Characteristics between $GaH_3 \cdot N(CH_3)_3$ and AHTEA for Representative Functiossnal Group

| | Gallane-trimethylamine | AHTEA |
|---|---|---|
| 1° Alcohol | ++ | ++ |
| 2° & 3° Alcohol | ++ | ++ |
| Phenol | ++ | ++ |
| Amine | ++ | ++ |
| Thiol | ++ | ++ |
| Aldehyde | + | ++ |
| Ketone | + | ++ |
| Quinone | + | + |
| Carboxylic acid | - | ++ |
| Acid anhydride | vvs | + |
| Acyl chloride | + | ++ |
| Ester | - | ++ |
| Lactone | - | ++ |
| Epoxide | - | ++ |
| Halide | - | - |
| Amide | vs | vvs |
| Nitrile | - | ++ |
| Nitrocompound | - | + |
| Azobenzene | s | vvs |
| Azoxybenzene | - | vvs |
| Isocynate | - | + |
| Pyridine | - | vs |
| Disulfide | vs | ++ |
| Sulfoxide | vs | ++ |
| Sulfone | - | - |
| Sulfonic acid | - | - |

++: Reaction completed in 1 h. +: Reaction completed in 6 h. s: Reaction completed in 12 h. vs: Reaction completed in 24 h. vvs: Reaction completed in over 72 h. -: sreaction did not proceed.

## Experimental

### Materials

All glassware were thoroughly dried in a drying oven and cooled down under a stream of dry nitrogen just prior to use. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. Gallium chloride (99.99% Aldrich Chem. Co) was used without further purification. Solvents were dried initially over calcium hydride and then decanted onto sodium under a nitrogen atmosphere. Benzophenone was added in the solvents and reflux was continued until the intense blue or purple color was evident. All reduction experiments were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer the solutions.

### Preparation of Reducing Agent

**Preparation of Lithium Gallium Hydride Solution.**[29] All glassware were thoroughly dried in a drying oven and cooled down under a stream of dry nitrogen just prior to use. In a 250 mL filter flask equipped with reflux condenser and containing a magnetic stirring bar were placed 2.77 g of finely powdered lithium hydride (348 mmol) and 10 mL of freshly distilled diethyl ether. A dropping funnel containing 5.14 g of gallium(III) chloride (29 mmol) in 20 mL of freshly distilled diethyl ether (dissolution is exothermic) was connected to the flask. The $LiH\text{-}(C_2H_5)_2O$ slurry was cooled to $-25$ °C to moderate the ensuing reaction with gallium(III) chloride, and the latter solution was added dropwise with stirring over a 1 h period. The reaction mixture was then warmed to room temperature and stirred for additional 5 h. The mixture was then filtered with a medium-porosity glass filter. Prior to use, this filter should be put through several purging cycles to remove moisture. The filtrate was collected in a 100 mL flask containing a magnetic stirring bar. The hydride concentration was determined by injection into a 2 N $H_2SO_4$-THF, diethyl ether, $H_2O$ (1 : 1 : 2) mixture to hydrolyzed the hydride.

**Preparation of Gallane-Trimethylamine Solution**[31,32]. Trimethylamine hydrochloride (0.67 g, 7.0 mmol) was added dropwise at $-78$ °C to lithium gallium hydride (0.43 g, 6.4 mmol) dissolved in ether. After the reaction subsided, the mixture was stirred for 2 h. LiCl was filtered off and solvent was removed under vacuum at a temperature ranging from $-78$ to $-45$ °C. The solid residue was sublimed from a trap at room temperature into a trap held at $-78$ °C. And trimethylamine-gallane was dissolved in THF.

### Procedure for Rate and Stoichiometry Studies

The procedure adopted was to add 1.33 mmol of the gallane-trimethylamine to 1.0 mmol of the organic compound in sufficient tetrahydrofuran to give 8 mL of solution. This makes the reaction mixture 0.167 M in gallane-trimethylamine (*i.e.*, 0.5 M in hydride) and 0.125 M in the compound under examination. The solution was maintained at 0 °C and aliquots were removed at appropriate intervals and analyzed for residual hydride. In this manner it was possible to establish both the rate at which reduction proceeds and the stoichiometry of the reaction, *i.e.*, the number of hydrides utilized per mole of compound when the reaction comes to an effective halt.

### Product Identification

For the most part, we adopted Brown's method.[1] The hydride consumption was used as an indicator for reduction. In some cases, GLC methods were utilized for the identification of products. Naphthalene was used as an internal standard. The columns used were 10% Carbowax 20 M and 10% SE-30, 7 ft × 0.125 in..

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# Activation Energy for the Decapsulation of Small Molecules from A-Type Zeolites

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Potential energy function sets for some ion-exchanged A-type zeolites, K-A and $Rb_{11}Na_1$-A, were determined by introducing the X-ray crystal structures as constraints. The potential functions reproduced well the X-ray crystal structures of the monovalent ion-exchanged zeolites. The activation energies for the en- or decapsulation of small molecules ($H_2$, $O_2$, $N_2$, and $CH_4$) and inert gases from the α-cage of model zeolites (Na-A, K-A, $Rb_{11}Na_1$-A, and $Cs_3Na_9$-A) were obtained by the molecular mechanical calculations. The calculated activation energies agreed well with experimental results.

## Introduction

Zeolites are well known for their industrial applications as catalysts, adsorbents, and molecular sieves. One of the practical applications of zeolites is to use those as a storage vessel for small gas molecules.[1-11] A small molecule whose kinetic diameter is a little larger than the opened window of a zeolite can be encapsulated by being compelled into the pores at high pressure and elevated temperature and then by cooling the system to room temperature and by depressurizing. This kind of phenomena, zeolitic encapsulation, was reported by Sesny and Shaffer.[8] They found that K-A zeolites can efficiently trap large amounts of small nonpolar molecules. Fraenkel *et al.*[4] showed experimentally that the diffusion parameters depend on both of the radius of alkali cation, M, which blocks the eight-ring window and the kinetic diameter of the encapsulated molecule.

Dehydrated A type zeolite ($M_xNa_{12-x}Si_{12}Al_{12}O_{48}$) has one large cavity, α-cage, per pseudo unit cell. This α-cage is

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