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OXIDATIVE ADDITION REACTIONS OF GROUP III METALS IN LOW OXIDATION STATES

II*. REACTIONS OF Ga_2X_4 WITH METHYL AND ETHYL HALIDES

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SUMMARY

The reactions between Ga_2X_4 (X = Cl, Br, I) and RX (R = Me, Et) are described. All the gallium halides undergo oxidative addition with methyl bromide and iodide, but only Ga_2Br_4 and Ga_2I_4 react with methyl chloride and in these cases extensive halogen exchange occurs. Isolable compounds include $CH_3Ga_2X_5$ (X=Cl, Br, I), $CH_3Ga_2Cl_4I$, and $CH_3Ga_2Br_4I$.

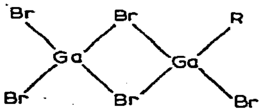
Reactions with ethyl halides are similar although the products are difficult to isolate since they are readily decomposed by ethyl halide.

The products of reaction have been characterised by Raman, IR, ^1H NMR and mass spectra, and observed trends are discussed.

INTRODUCTION

In previous work[1] we determined the reactivity of a series of alkyl bromides with Ga_2Br_4. We found that although reaction occurs with all of the alkyl halides studied, only for the lower members, *i.e.* methyl and ethyl, are tractable compounds formed, and in these cases the oxidative addition reactions may be represented:

$$RBr + Ga_2Br_4 \rightarrow RGa_2Br_5 \text{ (structure I).}$$



(I)

The present work was undertaken to determine within these systems, what effects a change of halide, *i.e.* Cl, Br, and I, of both alkyl and gallium compounds has on the reactivity.

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* For Part I see ref. 1.

RESULTS AND DISCUSSION

Reactions of gallium dihalides with methyl halides

With the exception of Ga_2Cl_4, which does not react with methyl chloride, all the gallium halides undergo addition reactions with the methyl halides. In order to minimise halogen exchange and possible further reaction of the products with excess methyl halide, the reactants were kept cold (−20°) throughout. While certain reactions proceed rapidly at these temperatures, others react exceedingly slowly, and even on warming to room temperature dissolution takes hours and the products are not those expected on the basis of simple oxidative addition of methyl halide to gallium dihalide, *i.e.*, $RY + Ga_2X_4 \rightarrow RGa_2X_4Y$. The reactions are therefore classified into two types.

(1). *Reactions giving expected products.* After the quick dissolution of the dihalides at −20° and removal of excess alkyl halide, the products analysed essentially as shown. In reactions (1) and (2), in which halogen exchange was possible, it was only found to a small extent. A little exchange in such cases is to be expected since Brown[3] found that gallium trichloride exchanged halogen with methyl bromide to an extent of 2% in 24 h at −80°.

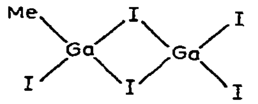
$$Ga_2Cl_4 + MeI \rightarrow MeGa_2Cl_4I \quad \text{(ref. 2)} \tag{1}$$

$$Ga_2Br_4 + MeI \rightarrow MeGa_2Br_4I \tag{2}$$

$$Ga_2Br_4 + MeBr \rightarrow MeGa_2Br_5 \quad \text{(ref. 1)} \tag{3}$$

$$Ga_2I_4 + MeI \rightarrow MeGa_2I_5 \tag{4}$$

The product of reaction (4), *i.e.* $MeGa_2I_5$, is thought to be a pure compound and not a mixture of the compounds Ga_2I_6 and $Ga_2I_4Me_2$. A strong Raman band at 55 cm^{-1} would be expected if Ga_2I_6 were present, and this band was absent in the Raman spectrum of product (4). This formulation is also supported by the mass spectrum. The structure of this compound would be expected to be similar to that proposed for the bromide analogue, *i.e.* as shown in (II).



(II)

The structures of products from reactions (1) and (2) are considered to be similar from spectroscopic evidence, which is discussed below.

(2). *Reactions giving exchanged products.* For reactions (5)–(7), complete dissolution of the dihalides took 3–4 h at room temperature. Immediately this had occurred, the residual methyl halide was removed to prevent further exchange. Spectroscopic and chemical analysis showed that extensive halogen exchange had occurred, and that the products were not those formed from the simple oxidative addition reaction, $Ga_2X_4 + RY \rightarrow RGa_2X_4Y$.

$$Ga_2I_4 + MeCl \rightarrow MeGa_2Cl_5 \tag{5}$$

$$Ga_2I_4 + MeBr \rightarrow MeGa_2Br_5 \tag{6}$$

$$Ga_2Br_4+MeCl \rightarrow MeGa_2Cl_{4.4}Br_{0.6} \qquad (7)$$

$$Ga_2Cl_4+MeBr \rightarrow MeGa_2Br_5 \qquad (8)$$

Reaction (5), in which complete halogen exchange occurs, provides a preparative method for $CH_3Ga_2Cl_5$, which could not be made by the reaction of gallium dichloride and methyl chloride.

Exchange may occur before and/or after oxidative addition, and whilst it is somewhat speculative to draw such conclusions from our observations, it seems likely that for reactions involving methyl chloride, initial exchange occurs, and is followed by oxidative addition with the methyl halide produced in the exchange reaction. This is supported by the observation that methyl chloride does not react with gallium dichloride. The postulated reaction sequence for the Ga_2Br_4/MeCl reaction is given below:

$$\begin{tikzcd}
Ga_2Br_4+n\,MeCl \arrow[r] & Ga_2Cl_nBr_{4-n}+n\,MeBr \arrow[d, "MeBr"] & \\
& MeGa_2Cl_nBr_{5-n} \arrow[r, "MeCl"] & MeGa_2Cl_5
\end{tikzcd}$$

Although in the above example the final product contained mixed halide, it would be expected that if the reaction time were extended further then complete exchange would occur.

While the slow reaction times for (5), (6), and (7) may be due in part to the very low solubilities of gallium dihalides in the respective methyl halides, the very different character of reaction (8) indicates that there are also other important factors in these complex reactions. In (8), at −20° Ga_2Cl_4 rapidly dissolved in methyl bromide. Immediately after dissolution, the excess methyl bromide was removed and the product examined. Surprisingly, the reaction was incomplete. Raman and mass spectra indicate that in addition to unchanged Ga_2Cl_4, the oxidised product $MeGa_2Cl_4Br$ was present. When the reaction mixture was allowed to stand for one hour at room temperature, the reaction was complete and the product consisted essentially of $MeGa_2Br_5$. In this case, extensive halogen exchange has occurred between the initial compound formed, $MeGa_2Cl_4Br$ and MeBr. The slowness of this reaction in solution was unexpected, since the similar reaction of Ga_2Br_4, which also was readily soluble in methyl bromide, gave a fully oxidised product immediately dissolution had occurred. The only obvious variable, since both halides are soluble, is the anion GaX_4^-. A possible mechanism is that solvation of the dihalides is followed by attack of methyl bromide on GaX_4^- to displace X^-:

$$MeBr+GaX_4^- \longrightarrow MeBr \longrightarrow GaX_3+X^-$$

TABLE 1

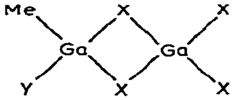
GALLIUM–CARBON STRETCHING VIBRATIONS IN METHYLGALLIUM HALIDES

Compound	*ν(Ga–C) (cm⁻¹)*	*Compound*	*ν(Ga–C) (cm⁻¹)*
$MeGa_2Cl_5$	609	$MeGa_2Cl_4I$	609
$MeGa_2Br_5$	596	$MeGa_2Br_4I$	599
$MeGa_2I_5$	577		

Since Ga^+ is likely to be unstable in the presence of halide ion, reaction with MeBr then occurs to give MeGaBrX and GaX_3 in solution. Subsequent removal of solvent could then give the proposed product. Since it is to be expected that Br^- will be more easily displaced than Cl^- from GaX_4^-, such a scheme may explain the differing reactivities.

Raman spectra. These are presented in the Experimental section and are consistent for compounds containing a gallium–carbon bond. It is instructive to compare ν(Ga–C) for the systems studied and these are given in Table 1.

The systems containing only one type of halogen, *i.e.* $MeGa_2X_5$ show a trend whereby ν(Ga–C) increases in the order $I < Br < Cl$, an order expected from a consideration of mass effects. Also in the systems $MeGa_2X_4Y$, whose structures are expected to be (III), the values of ν(Ga–C) are very similar to those of $MeGa_2X_5$.



(III)

This suggests that the values of ν(Ga–C) are related to those of the basic skeleton Ga_2X_4, and may therefore be used to identify the skeleton of an unknown compound. Thus in the reaction between methyl bromide and gallium dichloride already described an initial unidentified product was formed which gave a Raman band at 605 cm^{-1}. This suggests that the product has an $MeGa_2Cl_4$ skeleton and that the initial reaction was:

$$MeBr + Ga_2Cl_4 \rightarrow MeGa_2Cl_4Br$$

^1H NMR spectra. These were recorded in benzene solution and contain singlets at values of δ expected for compounds containing methyl groups attached to gallium. Although solvent effects cause these singlets to be concentration dependent, useful correlation ranges were observed, and are given in Table 2. It is seen that δ follows the order $MeGa_2Cl_4X < MeGa_2Br_4X < MeGa_2I_5$. This is the reverse of that expected from simple electronegativity considerations but is the same as that observed for the halomethylsilanes[4].

TABLE 2

CHEMICAL SHIFTS OF METHYLGALLIUM HALIDES

Compound	*δ (ppm)*	*Compound*	*δ (ppm)*	*Compound*	*δ (ppm)*
$MeGa_2Cl_5$ $MeGa_2Cl_4I$	0.30–0.46	$MeGa_2Br_5$ $MeGa_2Br_4I$	0.53–0.63	$MeGa_2I_5$	1.00–1.12

Mass spectra. The mass spectra contained peaks that show halogen exchange occurred in certain cases and confirm the results of analyses. For example, the products from the reaction of Ga_2I_4 with methyl chloride and bromide contain no iodine species confirming that halogen exchange in these reactions was virtually complete. In all cases molecular ion peaks were absent. However the observed peaks correspond to species consistent with the previously proposed fragmentation pattern[1], *i.e.* where the molecular ion loses either CH_3 or X followed by further fragmentation. Small peaks which cannot be explained by this fragmentation scheme are found in the mass spectra of those products which are known to have exchanged halogen only slightly. For example, $MeGa_2Br_4I$ contains peaks corresponding to the ions, GaI_3^+, GaI_2^+, and GaI_2Me^+. Since the product contains a small excess of iodine then these are to be expected.

Reactions with ethyl halides

Apart from the reaction between ethyl bromide and gallium dibromide, which has been described previously[1], these reactions did not yield pure products, since decomposition occurred in most cases even at low temperature. This is not surprising in view of the work of Brown *et al.*[5] who observed that solutions of gallium and aluminium trihalides readily evolved hydrogen halide even at low temperatures.

Reactions of ethyl bromide and iodide with the gallium dihalides all gave products which were often mixtures of yellow solids and oils when the reactions were carried out at −20° and below. Although the dihalides reacted without decomposition, the last traces of ethyl halide were difficult to remove quickly and it was at this stage that some decomposition occurred. It was thus not possible to obtain significant analytical data. Despite this decomposition, and the fact that in some cases extensive halogen exchange occurred, spectroscopic measurements give a good indication of the main products formed. The reactions of ethyl chloride with the gallium dihalides were not investigated since the corresponding reactions with methyl chloride took hours to complete, and any ethyl product formed over such a period would be expected to undergo complete decomposition.

Raman spectra. The Raman spectra of the products are given in Table 3. The gallium–carbon stretching vibrations for the products of the reaction of gallium dichloride and diiodide with ethyl bromide are very similar to those of $EtGa_2Br_5$, showing that extensive halogen exchange has occurred. The gallium diiodide/ethyl iodide reaction product gives a band at 548 cm^{-1}, the lowest observed for the series. It is to be expected that ν(Ga–C) will increase in the order $EtGa_2I_5 < EtGa_2Br_5 < EtGa_2Cl_5$, as was observed in the analogous methyl series, and the low band indicates that $EtGa_2I_5$ is formed in the reaction.

TABLE 3

GALLIUM–CARBON STRETCHING VIBRATIONS OF REACTION PRODUCTS (cm^{-1})

EtX	*Ga_2Cl_4*	*Ga_2Br_4*	*Ga_2I_4*
EtBr	564	562 (ref. 1)	561
EtI	570	556	548

The reaction product of Ga_2Cl_4 and EtI has the highest observed stretching vibration, which indicates a very high chlorine content, possibly $EtGa_2Cl_4I$. The product from the Ga_2Br_4/EtI reaction has a stretching vibration which is midway between those of $EtGa_2Br_5$ and the postulated $EtGa_2I_5$. We think, therefore, that considerable halogen exchange has occurred, but that neither bromine nor iodine is the predominant halogen.

Mass spectra. These are complicated by the presence of decomposition products arising rom a reaction between $EtGa_2X_5$ and EtX. However, in the main they support the conclusions reacted from the Raman spectra; *e.g.*, the mass spectra of the products of reactions between Ga_2Cl_4 and Ga_2Br_4 with EtBr contain peaks of mass corresponding to $EtGa_2Br_4^+$ suggesting that these products are mainly $EtGa_2Br_4X$ (X = Cl, Br, I).

^1H NMR spectra. These are all very similar with a complex multiplet at approximately δ 1 ppm indicating that the products contain a gallium-ethyl group. The shape of the multiplets does not change significantly from one product to another and no correlation may be drawn between the products and peaks for these A_2B_3 systems.

EXPERIMENTAL

Ga_2Cl_4 and Ga_2Br_4 were prepared by the methods previously described[6]. Ga_2I_4 was prepared by heating a mixture of Ga_2I_6 and Ga in exact stoichiometric quantities at 250° for 10 h.

The alkyl halides were purified by passing through an activated alumina column followed by fractional distillation. All reactions were carried out *in vacuo*. Detailed spectra are only given for reaction products, which from analytical data contain elements in stoichiometric amounts.

Reaction $Ga_2I_4 + MeI \longrightarrow MeGa_2I_5$

$MeGa_2I_5$, m.p. 99.1° (decomp.). (Found: C, 1.6; H, 0.6; Ga, 17.8; I, 80.3. $CH_3Ga_2I_5$ calcd.: C, 1.5; H, 0.4; Ga, 17.7; I, 80.4%.) Raman spectrum of solid (cm^{-1}): 2910 w, 1192 w, 577 m ν(Ga–C), 270 w, 143 s, 87 m. IR (nujol mull): 576 m ν(Ga–C), 364 m, 273 m, 230 w. Mass spectrum (relative intensities are in parentheses), *m/e*: $Ga_2I_5^+$ (0.1), 773; $Ga_2I_4Me^+$ (0.1), 661; $Ga_2I_3^+$ (0.1), 519; GaI_3^+ (17), 450; GaI_2Me^+ (31), 338; GaI_2^+ (4), 323; $GaIMe^+$ (100), 211; GaI^+ (57), 196; I^+ (96), 127; Ga^+ (80), 69.

Reaction $Ga_2I_4 + MeCl \longrightarrow MeGa_2Cl_5$

$MeGa_2Cl_5$, m.p. 65.1–67.1°. (Found: Ga, 42.3. $CH_3Ga_2Cl_5$ calcd.: Ga, 42.1%.) Raman spectrum of solid (cm^{-1}): 2917 w, 1222 w, 1202 w, 609 m ν(Ga–C), 401 w, 338 w, 160 w, 128 w, 95 vw. Mass spectrum: $Ga_2Cl_5^+$ (3), 313; $Ga_2Cl_4Me^+$ (2), 293; $GaCl_3^+$ (6), 174; $GaCl_2Me^+$ (21), 154; $GaClMe^+$ (100), 119; $GaCl^+$ (84), 104; $GaMe^+$ (6), 84; Ga^+ (12), 69.

Reaction $Ga_2Cl_4 + MeI \longrightarrow MeGa_2Cl_4I$

$MeGa_2Cl_4I$, m.p. 43.4–45.3°. (Found: C, 2.5; H, 0.7; Cl, 33.2; Ga, 32.8; I, 29.7. CH_3Cl_4GaI calcd.: C, 2.8; H, 0.7; Cl, 33.5; Ga, 32.9; I, 30.0%.) Raman spectrum of solid: 2912 w, 1202 w, 609 m ν(Ga–C), 576 vw, 289 w, 240 w, 209 s, 147 m, 111 w. IR (nujol mull) 607 m ν(Ga–C). The mass spectrum, in addition to containing expected peaks corresponding to $MeGa_2Cl_3I^+$, $Ga_2Cl_4I^+$, and $MeGa_2Cl_4^+$ had small peaks corresponding to GaI_3^+. This may be due to decomposition in the vapour phase since we have observed that the white crystalline compound decomposes to give a yellow solid on sublimation.

Reaction $Ga_2Br_4 + MeI \rightarrow MeGa_2Br_4I$

$MeGa_2Br_4I$, m.p. 42.0–44.9°. (Found: Ga, 22.8. $CH_3Br_4Ga_2I$ calcd.: 23.2%.) Raman spectrum of solid: 2902 w, 1209 w, 1190 w, 599 m ν(Ga–C) 310 w, 284 m, 189 w, 169 m. IR 596 m ν(Ga–C), 304 w, 267 s. The mass spectrum was similar to that described above in that it contained the expected peaks corresponding to $Ga_2Br_4I^+$, $MeGa_2Br_3I^+$, and $MeGa_2Br_4^+$ and also "iodide excess" peaks, *e.g.* GaI_3^+. These may be due to decomposition as above or to a small amount of halogen exchange. This latter possibility is supported by the low gallium analysis.

Reaction $Ga_2I_4 + MeBr \rightarrow MeGa_2Br_5$

The reaction product gave Raman and mass spectra identical with those of $MeGa_2Br_5$[1].

Reaction of Ga_2Cl_4 *and MeBr*

Although rapid dissolution occurred, the reaction was slow and complete oxidation was only achieved after the mixture was allowed to stand at room temperature for 1 h. The final product had Raman and mass spectra identical to those of $MeGa_2Br_5$. The Raman spectrum of the incomplete reaction product had a band at 609 cm^{-1} suggesting that initially the following oxidative addition reaction had occurred: $Ga_2Cl_4 + MeBr \rightarrow MeGa_2Cl_4Br$. This is supported by the mass spectrum which contained peaks at masses corresponding to $MeGa_2Cl_4^+$, $Ga_2Cl_4Br^+$, and $MeGa_2Cl_3Br^+$.

Reaction of Ga_2Br_4 *and MeCl*

Considerable but incomplete exchange occurred in this reaction. The product analysed as $MeGa_2Cl_{4.4}Br_{0.6}$. A Raman band at 606 cm^{-1} and peaks in the mass spectrum corresponding to $MeGa_2Cl_4^+$ and $Ga_2Cl_4Br^+$ indicate that $MeGa_2Cl_4Br$ is a major component of the product.

Spectra

^1H NMR spectra were recorded on a Varian A60 spectrometer. IR, Raman and mass spectra were recorded on a Perkin–Elmer 225, Carey 81 and Varian CH7 spectrometers respectively.

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