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OXIDATIVE ADDITION REACTIONS OF GROUP III METALS IN LOW OXIDATION STATES. REACTIONS OF Ga_2Br_4 WITH ALKYL BROMIDES

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SUMMARY

The oxidative addition reactions of gallium "dibromide" with several primary, secondary and tertiary alkyl bromides, and bromides of the type $(CH_2)_nBr_2$ have been examined. Whilst all the organic halides readily react with Ga_2Br_4, only in two reactions, namely with methyl and ethyl bromides are isolatable compounds produced and in these cases oxidative addition may be represented as:

$$Ga_2Br_4 + RBr \rightarrow RGa_2Br_5 .$$

Spectroscopic and other evidence indicates that these products are pure compounds rather than mixtures of the known compounds Ga_2Br_6 and $Ga_2Br_4R_2$.

INTRODUCTION

Group III metals in low oxidation(+I) states possess pairs of *s* valence electrons which may be used, with varying degrees of ease, to form the higher(+III) oxidation states. Of the metals, gallium, indium and thallium, which form stable +I oxidation states, the very strong reducing power of Ga^+, (*e.g.* it readily decomposes water to give hydrogen[1] and reduces carbon tetrachloride to carbon[2]) suggests that oxidative addition reactions will be particularly favourable.

Compounds containing Ga^I usually also contain Ga^{III}, *e.g.* the so called dihalides. These compounds readily undergo oxidative addition reactions with halogen:

$$X_2 + Ga^+GaX_4^- \rightarrow Ga_2X_6 \ (X=Cl, Br, I)$$

The ease with which these reactions proceed suggests the possibility of oxidative addition or insertion of Ga^+ into other covalent bonds of similar bond strengths to the halogens. It would be expected that the bond dissociation energy of X_2 would be an important factor affecting the ease of such an insertion, and since carbon–halogen bond strengths are similar in magnitude to those of the halogens, we chose to examine reactions between gallium "dihalides" and alkyl halides.

We have previously briefly reported the oxidative addition reaction between methyl iodide and Ga_2Cl_4[3]. Since such mixed halogen systems are subject to halogen exchange and present analytical difficulties, in order to study the range of alkyl halides which undergo such reactions, we here consider reactions between alkyl bromides and Ga_2Br_4.

RESULTS AND DISCUSSION

These will be considered in two parts:

(1). Products formed from the reaction of Ga_2Br_4 with methyl and ethyl bromides.

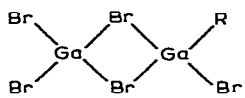
(2). Those formed from Ga_2Br_4 with n-propyl, n-butyl, benzyl, sec-propyl and tert-butyl bromides, 1,2-dibromoethane, 1,3-dibromopropane and 1,5-dibromopentane.

(1). The reactions proceeded rapidly and analysis shows that they may be represented as:

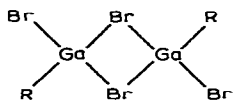
$$RBr + Ga_2Br_4 \rightarrow RGa_2Br_5 \ (R = Me,Et)$$

The compounds were low melting and the methyl compound readily sublimed. They exhibited no reducing properties which showed that oxidation had occurred and ruled out the possible but unlikely adducts $RBr \rightarrow Ga^+GaBr_4^-$. Further the 60 MHz ^1H NMR spectra are typical of alkyl groups bonded to gallium[4]. For the methyl compound $\delta = 1.00$ ppm in carbon tetrachloride solution, whilst the spectrum of the ethyl compound consists of an A_2B_3 multiplet centred at 1.40 ppm. This multiplet is partially resolved at 220 MHz and shows good agreement with the theoretically computed A_2B_3 spectrum.

It is likely that the products RGa_2Br_5 are either pure compounds of structure (I), which have not been previously reported, or mixtures of the known compounds Ga_2Br_6 and (II).



(I)



(II)

In an attempt to distinguish between these possibilities we have measured their vibrational and mass spectra.

Vibrational spectra

These are given in Table 1 together with those of $Ga_2Br_4Me_2$ and Ga_2Br_6 for comparison.

The IR spectrum of $Ga_2Br_4Me_2$ has been previously examined by Schmidbaur and Findeiss[4]. Their spectrum contained a strong band at 582 cm^{-1} which was assigned to ν(Ga–C). Our spectrum of the same compound shows a medium band, which we assign ν(Ga–C) at 591 cm^{-1}. On hydrolysis this band weakened and a band grew at 582 cm^{-1}; eventually only a band at 582 cm^{-1} remained. The previously reported spectrum is clearly that of the hydrolysed sample.

Although the spectra of $MeGa_2Br_5$ contain bands which are complimentary to both $Ga_2Br_4Me_2$ and Ga_2Br_6 there are distinct differences. In particular the IR spectrum of $MeGa_2Br_5$ contains a set of bands at 298, 306, and 326 cm^{-1} which are absent in the other spectra. Further the strongest band in the Raman spectrum of solid Ga_2Br_6 appears at 72 cm^{-1} and it would be expected that if the the reaction product were a mixture of $Ga_2Br_4Me_2$ and Ga_2Br_6 then this band should appear

TABLE 1

VIBRATIONAL SPECTRA[a]

$Ga_2Br_4Me_2$		$MeGa_2Br_5$		Ga_2Br_6	
Raman	IR	Raman	IR	Raman	IR[b]
2931 w		2930 w			
2900 w		2903 w			
		1208 m			
1203 w					
		1182 w			
595 m	591 m ν(Ga–C)	595 m	595 m ν(Ga–C)		347 s
			343 w	343 w	
				338 w	
	333 w	333 w			
			326 m		
			306 s		
			298 s		
		289 m		289 m	
278 m	278 m				
			273 s		
					268 s
	263 m				
	253 w				
	245 w				
				242 w	
					232 s
			222 m		
211 s					
		205 s		203 s	
164 w					
				157 w	
		143 m			
142 m				119 m	
		118 m			
110 m					
		98 w			
87 w					
				83 m	
		80 m			
				72 vs	

[a] Raman spectra were recorded on solid samples and IR on nujol mulls. [b] Taken from ref. 5.

strongly. In fact this band is absent in the Raman spectrum of $MeGa_2Br_5$. We conclude from these data that a pure compound (I) has been formed in the reaction.

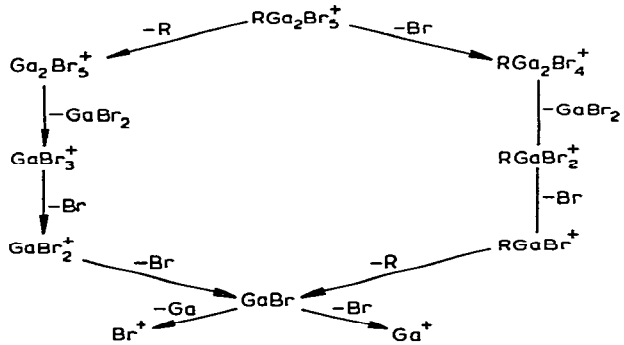
The notable features of the $EtGa_2Br_5$ spectra (for details see the experimental section) are a strong band at 562 cm^{-1}, which is characteristic of an ethyl group attached to gallium[4] and the absence of a band at 72 cm^{-1}, which again is a good indication that a pure compound is formed in the reaction.

Mass spectra

The mass spectra of $MeGa_2Br_5$ and $EtGa_2Br_5$ are given in the experimental

section together with that of $Ga_2Br_4Me_2$ for comparison. They consist of multiplets since both bromine and gallium exist in two isotopic forms. The mass numbers listed refer to the lowest mass number of each group of related peaks in such a multiplet. A molecular ion peak was observed for the ethyl compound but not for the methyl compounds.

The spectra are consistent with structure (I) and the proposed fragmentation patterns are shown below.



The mass spectrum of $Ga_2Br_4Me_2$ contains in addition to those shown above a peak corresponding to the species $Ga_2Br_3Me_2^+$.

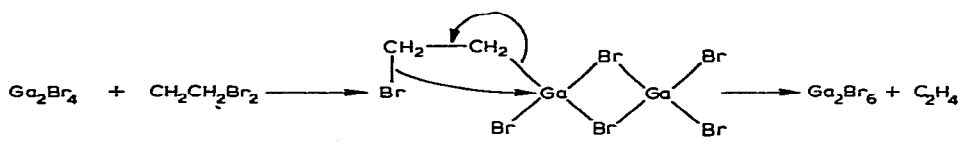
Mass spectral data thus also provide good evidence that compounds (I) are produced in the reaction.

Reactions with other halides

The reactions between Ga_2Br_4 and the other halides listed above were all very rapid and red oils were produced. These results are to be anticipated since previous work on the reactions between $RAlX_2$ and alkyl halides[7], and a study of gallium trihalide–alkyl halide complexes[6], has shown that for higher primary, secondary, and tertiary alkyl halides decomposition occurs and oils are produced.

In these cases it appears that oxidative addition reactions result in the formation of compounds similar to those formed by methyl and ethyl bromides, but their further reaction with excess alkyl halide results in the decomposition of these compounds.

Evidence for these intermediate compounds is provided by the reaction between Ga_2Br_4 and 1,2-dibromoethane. Here amounts of ethylene are also produced. The mass spectrum of the residue contains a peak corresponding to the species $Ga_2Br_5C_2H_4$. This does suggest that oxidative addition has occurred to produce (III) followed by the ready decomposition, the mechanism of which is also indicated.



(III)

EXPERIMENTAL

Ga_2Br_4 was prepared by the method previously described[8]. The Ga_2Br_4–alkyl bromide reactions were carried out *in vacuo* in an all glass apparatus which consisted of a main reaction vessel which had attached to it several side arms and an NMR tube. An excess of alkyl bromide was condensed on to the Ga_2Br_4 and immediately complete dissolution had occurred the excess was removed.

$MeGa_2Br_5$, m.p. 77.2–78.6°. (Found: C, 2.1; H, 0.6; Br, 72.0; Ga, 25.1. $CH_3Br_5Ga_2$ calcd.: C, 2.17; H, 0.55; Br, 72.1; Ga, 25.1%.) $EtGa_2Br_5$, m.p. 42.5–43.6°. (Found: C, 3.8; H, 1.0; Br, 70.3; Ga, 24.8. $C_2H_5Br_5Ga_2$ calcd.: C, 4.2; H, 0.89; Br, 70.3; Ga, 24.5%.) $Ga_2Br_4Me_2$ was prepared by the reaction of Ga_2Br_6 and $Si(CH_3)_4$ using the method previously described[4]. M.p. 72–74°. (Found: Ga, 28.5. $C_2H_6Br_4Ga_2$ calcd.: Ga, 28.5%.)

The alkyl halides were purified by passing through an activated alumina column and then fractional distillation. Final traces of water were removed by the addition of small amounts of "dibromide".

^1H NMR spectra were recorded on Varian A60 and HR-220 spectrometers. IR and Raman spectra were recorded on Perkin–Elmer 225 and Carey 81 spectrometers respectively. The Raman spectrum of $EtGa_2Br_5$(solid): 2930 w, 2917 w, 2877 w, 1196 w, 562 m ν(Ga–C), 333 w, 287 m, 209 s, 135 w, 118 w, 100 vw. The IR spectrum of $EtGa_2Br_5$: (nujol mull) 562 m ν(Ga–C), 365 w, 337 m, 311 m, 287 m, 271 m, 238 m.

The mass spectra, which are given below, were recorded on a Varian CH7 spectrometer. The mass spectrum of $MeGa_2Br_5$ (relative intensities are in parentheses); mass number 533 (1), 469 (1), 306 (8), 242 (8), 227 (58), 163 (50), 148 (36), 79 (78), 69 (100). The mass spectrum of $EtGa_2Br_5$: mass number 562 (0.1), 533 (1), 483 (1), 306 (20), 256 (17), 227 (100), 177 (15), 148 (15), 79 (14), 69 (16). The mass spectrum of $Ga_2Br_4Me_2$: mass number 533 (1), 469 (1), 405 (1), 306 (1), 242 (25), 227 (90), 163 (100), 148 (80), 79 (60), 69 (60).

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