Journal of Organometallic Chemistry, 81 (1974) 23—26

OXIDATIVE ADDITION REACTIONS OF GROUP III METALS IN LOW OXIDATION STATES

IV*. A STUDY OF REACTION INTERMEDIATES IN THE REACTION BETWEEN INDIUM MONOBROMIDE AND ALKYL BROMIDES

L G WATERWORTH and I J WORRALL
Department of Chemistry, The University, Lancaster (Great Britain)
(Received May 28th, 1974)

Summary

An investigation of the intermediates formed in the oxidative addition reactions between indium monobromide and alkyl halides is reported, and possible reaction schemes are formulated.

Introduction

Oxidative addition reactions of the indium monohalides (bromide and iodide) with alkyl halides are useful in the preparation of alkylindium dihalides [1]. The reactions are complex and several intermediates are formed particularly in those reactions between indium monobromide and alkyl bromides. In an attempt to obtain a better understanding of these complex reactions the present work was undertaken.

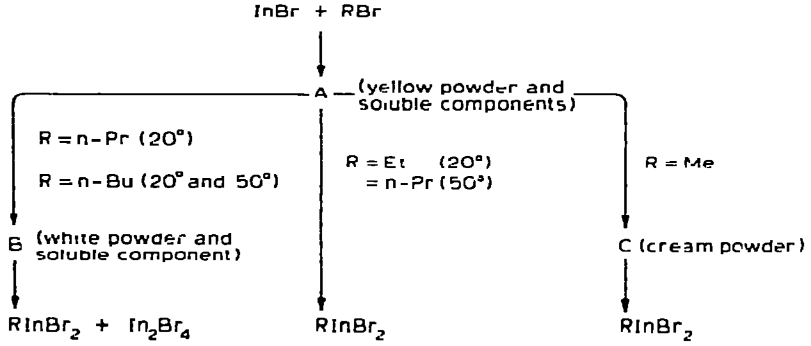
Results and discussion

The reactions investigated were those between indium monobromide and the alkyl bromides RBr (R = Me, Et, n-Pr, n-Bu). In every reaction compounds other than InBr and $RInBr_2$ could be distinguished Some of these were intermediates, others were side products. A reaction route could be determined in each case and these are summarised in Scheme 1. It may be seen that there are two types of reaction: those in which $RInBr_2$ is the only reaction product and those in which $RInBr_2$ is formed together with In_2Br_4. The reaction of n-propyl bromide falls into either category depending upon the temperature In the

---

[*] For Part III see ref 1

SCHEME 1



reactions where In_2Br_4 was a final product a white insoluble intermediate was also detected. Also in the methyl bromide reaction a cream insoluble intermediate was formed.

The intermediates will be considered and possible reaction schemes presented.

A Yellow powder and soluble components

(i) Yellow powder. This was produced as the first recognisable intermediate in each reaction. The time taken for the first traces of yellow to be visible in the orange powdered InBr was 1—2 days. The yellow powder was most readily obtained free of major contaminant (either InBr or final product) in the n-propyl and n-butyl bromide reactions, these being much slower than those of methyl or ethyl bromide. For this reason samples for detailed investigation were prepared from the former alkyl halides. Chemical analysis and Raman spectra have shown that the yellow intermediate is the new subhalide In_7Br_9 [2].

(ii) Soluble component produced with the yellow powder. In every case the soluble component consisted of $RInBr_2$ and R_2InBr probably present as the sesquihalide $R_3In_2Br_3$. The compounds were identified by their vibrational and mass spectra. The reactions so far may be therefore represented by eqn. 1:

$$9InBr + 3RBr \rightarrow In_7Br_9 + RInBr_2 + R_2InBr \quad (1)$$

It follows that in reactions where all the InBr is converted to $RInBr_2$ that the remaining reaction may be represented as eqn. 2.

$$In_7Br_9 + R_2InBr + 6RBr \rightarrow 8RInBr_2 \quad (2)$$

B White powder and soluble component

(i) White powder. This white powder was produced in the room temperature reaction of n-propyl bromide and in the reaction of n-butyl bromide at either room temperature or 50°. In appearance it was indistinguishable from In_2Br_4 but it could be readily identified as In_5Br_7 by chemical analysis and its distinctive intense Raman band at 139 cm^{-1} [3].

(ii) Soluble component. This was identified as $RInBr_2$ by Raman spectroscopy. The compound B may therefore be considered to be formed by the reaction 3 and this was confirmed by independent reactions described below.

$$In_7Br_9 + 2RBr \rightarrow In_5Br_7 + 2RInBr_2 \quad (3)$$

The final products are then formed in the slower reaction (eqn. 4), but the

$$In_5Br_7 + 3RBr \rightarrow 3RInBr_2 + In_2Br_4 \qquad (4)$$

possibility that In_5Br_7 may be formed in all reactions must also be considered. If this is so then for the methyl and ethyl bromide reactions, where complete conversion of InBr to $RInBr_2$ occurs and where In_5Br_7 is not isolable the rapid reaction $In_5Br_7 + R_2InBr + 4RBr \rightarrow 6RInBr_2$ must take place To test these possibilities the reactions were therefore set up independently, but they proceeded slowly, as shown, indicating that the intermediate In_5Br_7 is not formed in these reactions

$$In_5Br_7 + 3RBr \rightarrow 3RInBr_2 + In_2Br_4$$

Reactions between In_7Br_9 and RBr

These were carried out to test eqn. 3. In all cases a white powder was formed, after about one week, which was shown to be In_5Br_7 by Raman spectroscopy. This reacted further to give In_2Br_4 and $RInBr_2$ These reactions thus confirm eqns. 3 and 4 and show that there is a potential competition between eqns. 2 and 3. As the reactions between InBr and ethyl and methyl bromide give 100% $RInBr_2$ it also shows that in these cases reaction 2 is kinetically favoured. Competition between reactions 2 and 3 would also explain why the products obtained for n-propyl bromide are temperature dependent

Reactions of In_5Br_7 with n-propyl and n-butyl bromide

These were investigated to confirm that the formation of In_2Br_4 from In_5Br_7 results from the reaction of the latter with alkyl bromide In both cases In_2Br_4 and $RInBr_2$ were formed after a period of two weeks.

In summary, the reactions between indium monobromide and alkyl bromide may be represented by the following four stages

$$8InBr + 2RBr \rightarrow In_7Br_9 + R_2InBr \qquad (a)$$
$$In_7Br_9 + R_2InBr + 6RBr \rightarrow 8RInBr_2 \qquad (b)$$
$$In_7Br_9 + 2RBr \rightarrow In_5Br_7 + 2RInBr_2 \qquad (c)$$
$$In_5Br_7 + 3RBr \rightarrow 3RInBr_2 + In_2Br_4 \qquad (d)$$

Stages (b) and (c) appear to be competitive with (b) dominant for the smaller alkyl halides EtBr and MeBr and also for n-PrBr at 50°. Stage (c) is dominant for n-PrBr and n-BuBr.

A further cream intermediate C may be isolated from the InBr/MeBr reaction. This was isolated in small amounts in the presence of InBr and In_7Br_9 Chemical analysis showed it to have the composition In_2Br_3Me. This suggests that the intermediate might be the ionic species $In^+InBr_3Me^-$. The vibrational spectrum of this intermediate was recorded together with that of the salt $(NBu_4)^+InMeBr_3^-$ for comparison. The spectra are shown in Table 1

The main difference in the spectra is an additional band at 522 cm^{-1} in the indium—carbon region for the intermediate. We first of all thought that this was an impurity band from $MeInBr_2$, the final product of the reaction However, the band observed at 523 cm^{-1} in the spectrum of $MeInBr_2$ is always associated

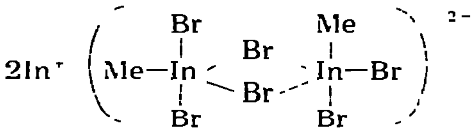
TABLE 1

VIBRATIONAL SPECTRA (cm^{-1}) OF In_3Br_3Me AND $(NBu_4)^+InMeBr_3^-$

In_2Br_3Me			$(NBu_4)^+InBr_3Me^-$	
Raman		IR	Raman	IR
196 s	ν(In—Br)		202 s	
510 s 523 s	ν(In—C)	508 m 522 m	507 s	507 m
1135 1144	δ(CH_3)			

with one [δ(CH_3)] at 1160 cm^{-1} which is absent in the spectrum of the intermediate The spectra therefore tend to rule out the simple ionic formulation.

Chemically, the intermediate has properties typical of lower-valent compounds, e.g. it reacts with water or ether to produce InBr (Cf. $In_2Br_4 + Et_2O \rightarrow InBr + InBr_3 \cdot OEt_2$). This suggests that the white intermediate contains indium(I) On this assumption a possible formulation consistent with the spectrum is given below



Experimental

The preparation of indium monobromide and the purification of alkyl halides have been previously described [1]. All reactions were carried out in vacuo and reaction intermediates and products were identified by chemical analysis and Raman vibrational spectra. IR and Raman spectra were recorded on Perkin—Elmer 225 and Carey 81 spectrometers respectively. The salt, $(NBu_4)^+InBr_3Me^-$, was prepared by reacting molar quantities of $MeInBr_2$ and NBu_4Br in dry methanol It was recrystallised as white needles from methanol in a dry box. (Analysis found· Br, 39.33; In, 18.49%, $C_{17}H_{39}BrInN$ calcd.. Br, 39.17, In, 18 76%)

References

1 M J S Gynane, L G Waterworth and I J Worrall, J Organometal Chem , 43 (1972) 257
2 L G Waterworth and I J Worrall Inorg. Nucl. Chem Lett , 9 (1973) 257
3 L G Waterworth and I J Worrall, J Inorg Nucl Chem , in press