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OXIDATIVE ADDITION REACTIONS OF GROUP III METALS IN LOW OXIDATION STATES

V*. REACTIONS OF INDIUM METAL WITH ALKYL HALIDES

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Summary

The reactions between indium metal and the alkyl halides RX (X = Br, I; R = Me, Et, n-Pr, n-Bu) are described. Spectroscopic evidence indicates that pure sesquihalides $R_3In_2X_3$ are formed in most cases. Convenient synthetic methods for some dialkylindium halides are also described.

Introduction

In a previous communication [1] we reported the synthesis of alkylindium halides by the direct reaction between the metal and alkyl halide. In this paper these reactions are extended, and where possible the nature of the products determined.

Results and discussion

The reactions investigated were those between indium metal and the organic halides RX, for X = Br, I, and R = Me, Et, n-Pr and n-Bu. All products had the composition $R_3In_2X_3$ and the reactions parallel the analogous aluminium reactions first reported by Van Gross and Maverty [3]. The products of these reactions are thought to be mixtures of $(R_2AlX)_2$, $(RAlX_2)_2$ and $R_3Al_2X_3$.

In an attempt to determine whether the products of the indium reactions are mixtures, or pure sesquihalides $R_3In_2X_3$ of structure I, their vibrational, mass and ^1H NMR spectra were recorded.

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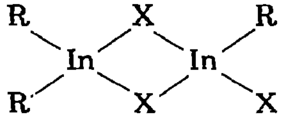
[*] For Part IV see ref. 2.



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Vibrational spectra

The methyl and ethyl compounds will be considered first. Their vibrational spectra in the indium—carbon and indium—halogen regions are given in Tables 1 and 2 together with those of the dialkyl and monoalkylindium halides for comparison.

For $Me_3In_2Br_3$ it is seen that in both the In—C and In—Br regions the spectra are similar to that expected for a 1/1 mixture of $MeInBr_2$ and Me_2InBr. Further the spectra observed on different parts of the sample showed marked variations in relative band intensity. It is clear that the reaction product consists of a mixture of mainly $MeInBr_2$ and Me_2InBr.

The spectrum of $Me_3In_2I_3$ differs markedly from that of the superimposed spectra of $MeInI_2$ and Me_2InI, and we propose that this is a pure compound of structure I. The indium—carbon vibrations give bands at 486, 509 and 555 cm^{-1}. The band at 509 cm^{-1} is assigned to ν(In—C) for the single terminal methyl group and the bands at 486 and 555 cm^{-1} to ν_{sym} and ν_{asym} of the Me_2In moiety. The latter bands show good agreement with those observed in dimethylindium iodide (558 and 488 cm^{-1}).

Two bands are observed in the indium—iodine region (above 100 cm^{-1}) of the spectrum as is to be expected for the dimeric structure I. The strong band at 153 cm^{-1} is assigned to the ring breathing mode and the medium band at 164 cm^{-1} to the terminal ν(In—I) mode.

The spectrum of the product obtained from the EtX/In reaction also differs from the spectra of the mixed compounds. For the bromide, differences are observed in both the In—C and In—Br regions whilst the iodide spectrum differs in the In—I region. For the bromide the bands at 460 and 520 cm^{-1} are assigned to the $\nu(In—C)_{sym}$ and $\nu(In—C)_{asym}$ stretch, and the band at 494 cm^{-1} to the single terminal ethyl group. Two bands are observed in the In—Br region consistent with structure I. The band at 194 cm^{-1} is comparable to that observed at 190 cm^{-1} in the spectrum of $InBr_3$ in the molten phase, and is assigned to the halogen bridging mode, whilst the band at 243 cm^{-1} is assigned to the terminal stretch. The main difference in the spectrum observed for the product of the EtI/In reaction and that of the mixed compounds occurs in the In—I region where two bands are observed and these may be assigned to bridging (147) and terminal (153 cm^{-1}) modes.

From these results we conclude that the pure compounds $Et_3In_2X_3$ (X = Br, I) are formed in the EtX/In reactions.

The spectra of the products of composition $R_3In_2X_3$ (R = n-Pr, n-Bu; X = Br, I) are complex and consist of broad bands. It is thus not possible to draw any firm conclusions about their nature. As previously reported [4], even for the n-propyl- and n-butylindium dihalides, the spectra are complex due to the presence of bands assignable to the different conformers, *trans* and *gauche* of

TABLE 1

VIBRATIONAL SPECTRA OF ALKYLINDIUM BROMIDES

Compound	ν(In—C)		ν(In—Br)
	Raman	IR	Raman
$Me_3In_2Br_3$	560vw, 524m, 518vw, 488s	557s, 524m, 485w	197m, 148m, 97m
$Et_3In_2Br_3$	520vw, 494s, 460s	529s, 500m, 458w	243w, 194s
n-$Pr_3In_2Br_3$	583s, 567s, 494s(br)	572m(br), 556m(br), 493s(br)	189m
n-$Bu_3In_2Br_3$	589s, 671s, 498s(br)	584s, 568m(br), 493s(br)	188s
$MeInBr_2$	524s, 517w	523s, 516m	196s, 148m, 97m
$EtInBr_2$	502m, 494s	496m, 491m	213s, 200s, 187s, 135w, 91w
n-$PrInBr_2$	584m(br), 495m(br)	578m(br), 490m(br)	188s(br)
n-$BuInBr_2$	584m(br), 495m(br)	583s(br), 496s(br)	232w, 189s
Me_2InBr	495vs	556s, 434vw	
Et_2InBr	510w, 459s	507s, 456s	
n-Pr_2InBr	579w, 565s, 496m(br)	584m, 496m	
n-Bu_2InBr	575m	590w, 568m	219m

TABLE 2

VIBRATIONAL SPECTRA OF ALKYLINDIUM IODIDES

Compound	ν(In—C)		ν(In—I)
	Raman	IR	Raman
$Me_3In_2I_3$	555w, 509s, 486s	553s, 505s, 484m	164m, 153s
$Et_3In_2I_3$	502w, 486s, 455s	503s, 486s, 450s	215w, 153s, 147s
n-$Pr_3In_2I_3$	575s, 563s, 488s(br)	573s(br), 557s(br), 484s(br)	146s
n-$Bu_3In_2I_3$	584m(br), 569m(br), 488m(br)	577m(br), 562m(br), 480m(br)	145s
$MeInI_2$	484s	555s	196w, 185m, 141s
$EtInI_2$	489s	484s	250w, 171m, 144s
n-$PrInI_2$	574s(br), 484s(br)	572s(br), 482m(br)	196w, 167m, 141s
n-$BuInI_2$	577m(br), 487m(br)	576s(br), 482m(br)	184m, 168m, 143s
Me_2InI	487s	550s, 481vw	
Et_2InI	506w, 456vs	502m, 454m	

the alkyl chains which give very different ν(In—C) bands. With two alkyl groups attached to the metal this complexity is increased since other conformers might also be expected, i.e. *trans—trans*, *gauche—gauche* and *trans—gauche*. Similar spectra of analogous tin compounds have been discussed by Cummins [5].

Mass spectra

The molecular ion peaks corresponding to $R_3In_2X_3^+$ were observed for the products of composition $Et_3In_2Br_3$, $Et_3In_2I_3$ and n-$Bu_3In_2I_3$; clearly in these cases pure sesquihalides are present in the vapour phase. For the remaining compounds, (apart from the n-propyl bromide compound for which satisfactory mass spectra could not be obtained) molecular ion peaks were absent.

We have previously recorded mass spectra of the monoalkylindium dihalides $RInX_2$ [4] and these all have peaks of significant intensity corresponding to mass numbers $RIn_2X_4^+$. Of the compounds examined in this work, apart from the product of composition $Me_3In_2Br_3$ which is discussed below, this peak was absent. This does suggest that the compounds $RInX_2$ are not present in the vapour and that the major components are the pure sesquihalides $R_3In_2X_3$. For the product of composition $Me_3In_2Br_3$ a significant peak was observed at mass number corresponding to the ion $MeInBr_4^+$, indicating that dimeric $Me_2In_2Br_4$ is present in the vapour which must therefore contain mixed compounds. This conclusion is in agreement with results obtained from vibrational spectra.

^{1}H NMR spectra

These were recorded in methylene chloride solution and details are given in the experimental section.

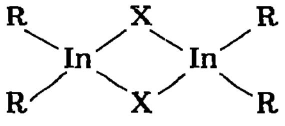
If the compounds have structure I then there are three environmentally different alkyl groups. The spectra of the ethyl, n-propyl and n-butyl compounds are complex and it is not possible to draw any firm conclusions. The methyl compounds give simple spectra at 40° which consist of two peaks with intensity ratio 2/1. These peaks may originate either from a sesquihalide of structure I in which rapid exchange occurs between the 1,1′-methyl groups, possibly by a halogen-bridge cleavage mechanism, or from mixed dialkyl and monoalkyl compounds. Similar spectra have been observed for analogous aluminium sesquihalides at ambient temperature. On cooling down to —70° resolution to the expected three band spectrum occurred [6]. With the methylindium compounds spectra were recorded down to —80°, and although broadening of the most intense band occurred for the iodide, no splitting was observed.

The results are therefore inconclusive.

Synthesis of dialkylindium halides

Known syntheses usually involve the somewhat tedious initial synthesis of the trialkylindiums followed by reaction with the appropriate quantity of indium trihalide. We found that the dialkylindium halides, R_2InX ($X = Br$, $R =$ Me, Et, n-Pr, n-Bu; $X = I$, $R =$ Me, Et), may be very conveniently synthesised from the sesquihalides by reaction with KBr or KI. Here use is made of the fact that dialkylindium halides are weaker Lewis acids than the monoalkyls, which are retained in complex form, and the volatile dialkyl compounds readily separated. Similar methods have been used for analogous aluminium compounds [7]. Details of the syntheses are given in the experimental section. Their vibrational spectra, of which the Raman have not been previously reported, are given in Tables 1 and 2.

It is generally thought, on the basis of solution molecular weight determinations [9] that these compounds have the dimeric structure II. It is seen that



(II)

for the dimethyl compounds halogen bands are absent in the Raman spectra. We are unable to state whether this is due to a spectroscopic curiosity or has structural significance, but it is tempting to postulate structures containing the ionic species $Me_2In^+X^-$ for these compounds in the solid phase since the In—C region of the spectra is very similar to that observed for $MeInI_2$ [4] which is thought to be $Me_2In^+InI_4^-$. Clearly a crystal structure determination is desirable to resolve this issue.

Experimental

The alkyl halides were purified by the method previously described [8]. All reactions were carried out in vacuo at ambient temperatures.

The analytical data are represented in Table 3.

TABLE 3

ANALYTICAL DATA OF $R_3In_2X_3$

Compound	Analysis found (calcd.) (%)		M.p. (°C)
	In	X	
$Me_3In_2Br_3$	44.90	46.70	98-102
	(44.63)	(46.60)	
$Et_3In_2Br_3$	41.41	42.84	63.5
	(41.21)	(43.09)	
n-$Pr_3In_2Br_3$	38.39	40.07	Liquid
	(38.31)	(40.16)	
n-$Bu_3In_2Br_3$	35.67	37.51	Liquid
	(35.85)	(37.42)	
$Me_3In_2I_3$	34.92	58.42	112-114
	(35.06)	(58.19)	
$Et_3In_2I_3$	32.61	54.48	72-75
	(32.94)	(54.59)	
n-$Pr_3In_2I_3$	31.20	51.41	Liquid
	(31.07)	(51.49)	
n-$Bu_3In_2I_3$	29.29	48.71	Liquid
	(29.40)	(48.75)	

^1H NMR spectra

These were recorded on a Varian HA 100-D spectrometer and in all cases refer to the solvent CH_2Cl_2 as standard.

$Me_3In_2I_3$. Two singlets at δ −4.19 and −4.37 ppm; intensity ratio 1/2.

$Et_3In_2I_3$. Sharp singlet at δ −3.92 ppm.

n-$Pr_3In_2I_3$. Complex second order spectrum. Two sets of peaks centred at δ −4.24 and −3.59 ppm; intensity ratio 3/4.

n-$Bu_3In_2I_3$. Complex second order spectrum. Two sets of peaks centred at δ −4.25 and −3.62 ppm; intensity ratio 1/2.

$Me_3In_2Br_3$. Two singlets at δ −4.63 and −4.73 ppm; intensity ratio 1/2.

$Et_3In_2Br_3$. Complex spectrum with multiplet centred at δ −3.97 ppm.

n-$Pr_3In_2Br_3$. Complex spectrum. Two sets of peaks centred at δ −4.22 and −3.42 ppm; integration ratio 3/4.

The dialkylindium halides were prepared by heating together equimolar quantities of sesquihalide and dry powdered potassium halide in vacuo at 80-100°; at these temperatures the dialkyl compounds sublimed away from the less volatile monoalkyl compounds.

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