Determination of the heat of formation of trimethylindium and calculation of the mean In-CH₃ bond dissociation energy

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The enthalpy of reaction of $In(CH_3)_3$, c with a chloroform solution of bromine is -162.5 kcal mole⁻¹. With this value $\Delta H_f^{0}_{298}[In(CH_3)_3,c] = 29.5$ kcal mole⁻¹ and $\Delta H_f^{0}_{298}[In(CH_3)_3,g] = 41.1$ kcal mole⁻¹. Combining the latter with $\Delta H_f^{0}_{298}[CH_3,g] = 33.2$ kcal mole⁻¹ and $\Delta H_f^{0}_{298}[In,g] = 58.2$ kcal mole⁻¹ then gives $E(In-CH_3) = 38.9$ kcal mole⁻¹. From previous kinetic studies $D[(CH_3)_2In-CH_3] + D[In-CH_3] = 87.9$ kcal mole⁻¹. Hence $D[CH_3In-CH_3] = 28.8$ kcal mole⁻¹.

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Introduction

The pyrolysis of trimethylindium has been studied in a toluene carrier system (1). From the kinetic data the following values were estimated: $D[(CH_3)_2In-CH_3] = 47.2 \text{ kcal mole}^{-1}$, $D[In-CH_3] = 40.7 \text{ kcal mole}^{-1}$. The kinetic mechanism proposed assumed that under all conditions used reaction [2] was much faster than reaction [1].

[1] $\operatorname{In}(\operatorname{CH}_3)_3 \to \operatorname{In}(\operatorname{CH}_3)_2 + \operatorname{CH}_3$

$$[2] \qquad In(CH_3)_2 \rightarrow InCH_3 + CH_3$$

The present work was undertaken to determine the mean metal-carbon bond dissociation energy in trimethylindium and hence $D[CH_3In-CH_3]$.

Fowell and Mortimer (2) used the reaction of trimethylgallium with excess iodine to determine the heat of formation of this alkyl. Because of the high strength of the gallium–carbon bond in methylgallium (3) only two methyl radicals were readily displaced. Concentrated iodine solution at an elevated temperature was required to obtain sufficient extent of reaction to allow the heat of formation of the alkyl to be determined. Bromine was chosen over iodine for the present work because a reliable value for $\Delta H_f^0_{298}$ (InBr₃, c) was available.

Experimental

Materials (a) Trimethylindium was prepared by refluxing indium metal with dimethylmercury in an atmosphere of dry nitrogen using mercuric chloride as catalyst (4). After 8 days the reaction flask was cooled to 0 °C (vapor pressure of trimethylindium, 0.2 mm) and the unreacted dimethylmercury (vapor pressure, 17 mm) was distilled off. The crude trimethylindium was transferred to the main alkyl

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storage system where the remaining dimethylmercury was removed by repeated degassing at 0 °C. The final product melted at 89.5 °C and gave vapor pressure measurements consistent with literature values (4). It was stored under its own vapor pressure at -190 °C.

(b) Chloroform and bromine were fractionally distilled and then degassed by bulb to bulb distillation. Sufficient bromine was vacuum distilled into chloroform to give approximately 1 N solution. The resulting solution was stored under a nitrogen atmosphere.

(c) InBr₃ was dried in a nitrogen atmosphere using phosphorus pentoxide.

Apparatus and Procedure

The apparatus used was similar to that of Fowell and Mortimer (2). The temperature rise was measured with a Beckman thermometer equipped with a magnifying lens so that the relative temperature could be estimated to within 0.001° . A 0.20 W bare wire chromel immersion heater was used for electrical calibration.

The normality of the bromine solution was checked before each run by addition of excess potassium iodide followed by titration of the liberated iodine with standard sodium thiosulfate. Similar titrations were used to determine the amount of bromine consumed in a run. Titrations before and after blank runs showed that no measurable loss of bromine occurs.

Trimethylindium was distilled under vacuum into a weighed ampul, sealed, and reweighed. The ampul was attached to a rod fitted into the reaction vessel through a ground glass sleeve. To start an experiment, the ampul was crushed against the bottom of the reaction vessel by depressing the rod. Blank runs showed that no measurable heat is generated when an empty evacuated ampul is broken.

Results and Discussion

The results are shown in Table I. All experiments were carried out at approximately 25 °C. Within the experimental scatter the observed heats of reaction are consistent with the percentage of the alkyl undergoing reaction. The data are limited, but inspection of Fig. 1 indicates a pattern of reaction similar to that previously observed by Fowell and Mortimer for the 1634

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FIG. 1. Variation of the heat of reaction of trimethylindium with bromine in chloroform solution at 25 °C. The percent reaction is based on replacement of all three methyl groups by bromine. Solid line, linear least mean squares line obtained using the points above 66% reaction; broken line, plot obtained if the first two methyl groups are readily replaced by bromine so that a linear relation-ship holds from 0-66.7% conversion.

TABLE I

Enthalpy of reaction of trimethylindium with bromine in chloroform solution

Sample weight (g)	Normality of Br ₂ solution*	Conversion†	$\Delta H_{\rm rx}$ (kcal mole ⁻¹)
0.0897	1.085	84	143
0.1043	0.972	78	139
0.0657	0.053	75	131
0.0907	0.656	71	132
0.1461	0.827	66	121
0.0805	0.658	65	116
0.1422	1.055	63	112

*25.0 ml bromine solution used in each run. †Based on replacement of all three methyl groups by bromine.

reaction of trimethylgallium with iodine (2), quantitative replacement of two methyl radicals by halogen followed by slow replacement of the third methyl group. The linear least mean squares extrapolation to 100% based on this mechanism gives $\Delta H = 162.5$ kcal mole⁻¹ for reaction [3].

[3] $In(CH_3)_3(c) + 3 Br_2(soln.) \rightarrow$

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 $InBr_3(soln.) + 3CH_3Br(g)$

No correction has been made for the heat of solution of any CH₃Br which remains in solution. The heat of solution of InBr₃,c in chloroform was determined in separate experiments as $\Delta H_{soln} = -1.4 \pm 0.3$ kcal mole⁻¹. The enthalpy of solution of bromine in chloroform is 0.7 kcal mole⁻¹ (5). With $\Delta H_{\ell}^{0}{}_{298}(\text{InBr}_{3},\text{c}) = -102.5$ kcal mole⁻¹ (6) and $\Delta H_{\ell}^{0}{}_{298}(\text{CH}_{3}\text{Br},\text{g}) = -9.0$ kcal mole⁻¹ (7), $\Delta H_{\ell}^{0}{}_{298}(\text{In(CH}_{3})_{3},\text{c}) = 29.5$ kcal mole⁻¹. Combining this with $\Delta H_{\text{sublimation}}$ $(In(CH_3)_{3,c}) = 11.6$ kcal mole⁻¹ (4) gives $\Delta H_f^{0}{}_{298}(In(CH_3)_{3,g}) = 41.1$ kcal mole⁻¹. With $\Delta H_{\rm f}({\rm CH}_3) = 33.2$ (5) and $\Delta H_{\rm f}({\rm In}_3{\rm g}) = 58.2$ (6) the mean metal-methyl bond dissociation energy in trimethylindium, $E(In-CH_3)$, is 38.9 kcal mole⁻¹. This gives $D[CH_3In-CH_3] = 28.8$ kcal mole⁻¹, a value consistent with the previously proposed kinetic mechanism for the decomposition of trimethylindium in a toluene carrier system (1).

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- 1. M. G. JACKO and S. J. W. PRICE. Can. J. Chem. 42. 1198 (1964).
- 2. P. A. FOWELL and C. T. MORTIMER. J. Chem. Soc. 3734 (1958).
- 3. M. G. JACKO and S. J. W. PRICE. Can. J. Chem. 41. 1560 (1963).
- 5.
- 1560 (1963).
 L. M. DENNIS, R. W. WORK, E. G. ROCKOW, and E. M. CHARMOT. J. Am. Chem. Soc. 56, 1047 (1934).
 Selected values of chemical thermodynamic properties.
 Natl. Bur. Std. U.S. Tech. Notes, No. 270-1 (1965).
 Selected values of chemical thermodynamic properties.
 Natl. Bur. Std. U.S. Tech. Notes, No. 270-2 (1965).
 P. FOWELL, J. R. LACHER, and J. D. PARK. Trans.
 Faraday Soc. 61, 1324 (1965). 7.