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Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Derivatives. III. The Trimethylindium–Amine System

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The exchange reactions on $In(CH_3)_3$–amine systems have been examined in both methylene chloride and methylcyclohexane solvents. When the base is trimethylamine or dimethylamine, the rate-determining step for the reaction is shown to be the dissociation of the addition compound. The rate law for this process can be expressed as $1/\tau_A = k_1[AB]/[A]$. The activation energies for these reactions are 19.7 ± 1.0 and 15.4 ± 0.6 kcal/mole, respectively. When the base is monomethylamine, the reaction proceeds through a displacement path having the rate laws: $1/\tau_A = k_1[AB]$ and $^1/\tau_{AB} = k_1[A]$. The activation energy for this process is 11.6 ± 0.1 kcal/mole. When excess base is present in solution, rapid exchange occurs in all cases at −60°.

In early papers of this series[2,3] the exchange reactions in trimethylgallium–Lewis base systems were examined. It was found that for trimethylgallium adducts of trimethylamine and dimethylamine, exchange of trimethylgallium molecules occurred through a unimolecular dissociation mechanism

$$(CH_3)_3Ga\cdot N(CH_3)_3 \rightleftharpoons (CH_3)_3Ga + N(CH_3)_3$$

However, when the steric bulk of the groups attached to the nitrogen atom was reduced, the ease of backside electrophilic substitution on the nitrogen atom was enhanced and the mechanism for exchange shifted from a dissociation mechanism to a bimolecular electrophilic displacement process. Thus, for the trimethylgallium adducts of monomethylamine and ammonia, the exchange could be represented by

$$(CH_3)_3Ga\cdot NH_2(CH_3) + (CH_3)_3Ga^* \rightleftharpoons (CH_3)_3Ga^*\cdot N(CH_3)H_2 + (CH_3)_3Ga$$

These findings were used to elucidate the mechanisms of exchange reactions studied earlier in the BF_3–base systems.[4,5]

The present study extends this investigation to include the addition compounds of trimethylindium with trimethylamine, dimethylamine, and monomethylamine, in order to investigate the effect of changing the Lewis acid on the mechanism of the reaction. The trimethylindium–ammonia system has not been studied because of the reported decomposition of the adduct at room temperature[6]

$$(CH_3)_3In\cdot NH_3 \rightleftharpoons [(CH_3)_2In\cdot NH_2]_2 + CH_4$$

Experimental Section

Trimethylindium was prepared by the action of dimethylmercury on indium metal,[7] with a trace of mercuric chloride as a catalyst. It was then purified by trap to trap vacuum sublimation with the trimethylindium retained in an ice–water trap. Dimethylmercury was obtained from the Eastman Organic Chemicals Co. and indium metal from the Allied Chemical Co. Hydrocarbon solvents and standards were refluxed over sodium metal, distilled, and stored in the vacuum line until used. Methylene chloride was dried by refluxing over barium oxide and also was stored under vacuum. The purity of all materials was determined by nmr spectroscopy.

Nmr samples were prepared by standard high-vacuum techniques. Trimethylindium concentrations were determined by weight, while the amounts of base were measured by gas–volume methods. A measured amount of solvent was added by distillation from a pipet. An equal amount of solvent (0.5 ml) was used in each sample to ensure that effects caused by changes in concentration due to changes in the density of the solvent at variable temperatures were minimized. A small amount of cyclopentane was used as an internal standard for nmr measurements.

Kinetic measurements and lifetimes were obtained by standard nmr line-broadening techniques.[8] In the region of slow exchange (*i.e.*, $\tau_A \gg (\omega_A - \omega_B)^{-1}$) the approximation[8,9] $1/\tau = \pi(\nu_{1/2} - \nu^0_{1/2})$ was used to calculate lifetimes, where $\nu_{1/2}$ is the width at half-height of the peak under exchange conditions and $\nu^0_{1/2}$ is the width at half-height when no exchange exists. In all cases the samples were examined over an extended temperature range. The spectra obtained at room temperature show a single absorption for the trimethylindium protons with the chemical shift dependent on the mole fraction of free trimethylindium. (Mole fraction as used here and throughout the text refers to the mole fraction of reacting species only.) At low temperatures (∼−60°) all samples showed two narrow ($\nu_{1/2} \sim 0.5$ cps) lines, one corresponding to the free trimethylindium and the second, high-field line corresponding to the methyl groups in the trimethylindium adduct. This behavior indicates that line broadening derived from chemical exchange should occur at intermediate temperatures.

The nmr spectra were obtained on a Varian A-60A spectrometer, equipped with a variable-temperature probe. Line positions were obtained by linear interpolation between audiofrequency side bands of cyclopentane. Broadened line widths were read off the chart paper with the linear calibration being checked by comparison with audiofrequency side bands.

Results and Discussion

In all systems containing excess trimethylindium, rapid exchange was demonstrated by the observation of a single nmr resonance line for the protons on the trimethylindium moieties. When excess amine was

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TABLE I

CONCENTRATION DEPENDENCE OF THE CHEMICAL SHIFT OF THE INDIUM METHYL PROTONS AND AMINE METHYL PROTONS AT AMBIENT TEMPERATURE

$In(CH_3)_3 \cdot N(CH_3)_3$				$In(CH_3)_3 \cdot NH(CH_3)_2$		$In(CH_3)_3 \cdot NH_2(CH_3)$	
$\delta_{In(CH_3)_3}$ [a,b]	P_A [c]	$\delta_{N(CH_3)_3}$ [a,b]	P_B [c]	$\delta_{In(CH_3)_3}$ [a,b]	P_A [c]	$\delta_{In(CH_3)_3}$ [a,d]	P_A [c]
1.55	1.000	−0.59	1.000	1.55	1.000	1.60	1.000
1.67	0.780	−0.65	0.540	1.65	0.698	1.70	0.763
1.70	0.692	−0.65	0.473	1.73	0.551	1.74	0.727
1.73	0.632	−0.68	0.311	1.76	0.478	1.74	0.641
1.76	0.501	−0.72	0.067	1.76	0.470	1.83	0.485
1.82	0.433	−0.73	0.000	1.80	0.432	1.88	0.389
1.85	0.305			1.82	0.411	1.91	0.241
1.90	0.197			1.87	0.272	2.00	0.094
1.98	0.097					2.04	0.000
1.99	0.000						

[a] Ppm from cyclopentane. [b] Methylcyclohexane solvent. [c] Mole fraction of the free acid or base. [d] Methylene chloride solvent.

present a single resonance was obtained for all amine methyl protons. The chemical shift of this coalesced peak exhibits a linear dependence on mole fraction, which is indicative of rapid exchange. These data are presented in Table I.

In order to determine the mechanism of exchange for these reactions concentration-dependence studies were carried out on the systems containing excess trimethylindium where the conditions of slow exchange are met; *i.e.*, the lifetimes of the free acid (τ_A) and the adduct (τ_{AB}) are large compared to the reciprocal of the chemical shift difference of the two compounds.[8] Under these conditions the lifetime (in radians/sec) may be found from the approximation $1/\tau = \pi(\nu_{1/2} - \nu^0_{1/2})$. Several samples containing excess base ($N(CH_3)_3$, $N(CH_3)_2H$, or $N(CH_3)H_2$) were also examined at low temperature ($<-60°$) but in all instances still showed rapid exchange thus preventing a determination of the mechanism of exchange under these conditions.

Table II shows the experimental values of $1/\tau_A$ and $1/\tau_{AB}$ for various concentrations of $In(CH_3)_3$ and $In(CH_3)_3 \cdot N(CH_3)_3$ in methylcyclohexane. It can readily be seen that the lifetime of the free $In(CH_3)_3$ is concentration dependent, while the lifetime of the adduct is constant within experimental error. This is consistent with a dissociation mechanism

$$In(CH_3)_3 \cdot N(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} In(CH_3)_3 + N(CH_3)_3$$

From the rate equation for this mechanism it can be shown that $1/\tau_A = k_1[(CH_3)_3In \cdot N(CH_3)_3]/[In(CH_3)_3]$ and $1/\tau_{AB} = k_1$. The values for k_1 obtained from these two expressions are given in columns 4 and 5 of Table II. The average values are 6.4 ± 1.0 and 7.2 ± 0.9 sec^{-1}, respectively, and are equal within experimental error.

The activation energy was obtained by a least-squares fit of an Arrhenius plot of log $(1/\tau_A)$ and log $(1/\tau_{AB})$ *vs.* $1/\tau$, over the range of temperatures in which the conditions of slow exchange were met (see Figure 1). The average of four values of the activation energy was 19.7 ± 1.0 kcal/mole. The literature value for the dissociation energy of the adduct is 19.9 ± 0.5 kcal/mole,[6] thereby supporting the postulated mechanism. The entropy of activation for this system is +21 eu as shown in Table III.

TABLE II

THE CONCENTRATION DEPENDENCE OF THE $In(CH_3)_3 \cdot N(CH_3)_3$ SYSTEM AT −17.5°

$[In(CH_3)_3]$, *M*	$[In(CH_3)_3 \cdot N(CH_3)_3]$, *M*	$1/\tau_A$, sec^{-1}	$1/\tau_{AB}$, sec^{-1}	$(1/\tau_A)/\{[In(CH_3)_3 \cdot N(CH_3)_3]/[In(CH_3)_3]\}$
0.101	0.029	2.4	5.8	8.6
0.072	0.033	2.7	5.2	6.0
0.070	0.069	6.8	6.8	6.9
0.062	0.081	10.1	5.8	7.7
0.054	0.123	17.2	7.4	7.5
0.064	0.259	27.4	7.6	6.7
			Av 6.4 ± 1.0	Av 7.2 ± 0.9

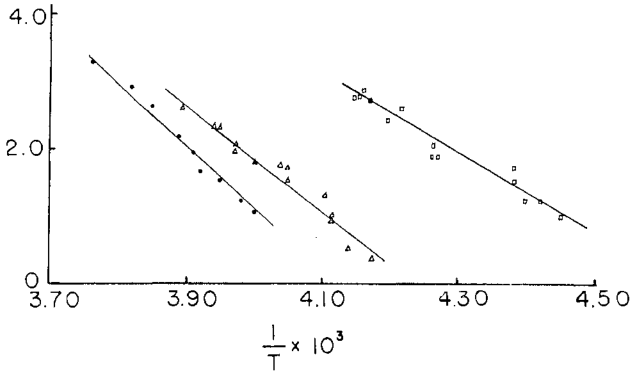

Figure 1.—Arrhenius plots for the activation energy. Log $(1/\tau)$ *vs.* $1/T$(°K) for: ●, $In(CH_3)_3 \cdot N(CH_3)_3$ system, $\Delta E^\ddagger$ = 19.7 ± 1 kcal/mole; △, $In(CH_3)_3 \cdot NH(CH_3)_2$ system, $\Delta E^\ddagger$ = 15.4 ± 0.6 kcal/mole; □, $In(CH_3)_3 \cdot NH_2(CH_3)$ system, $\Delta E^\ddagger$ = 11.6 ± 0.1 kcal/mole.

The dissociation mechanism was also observed for the $In(CH_3)_3 \cdot N(CH_3)_2H$ system, with the data given in Table IV.

Values for k_1 calculated from columns 4 and 5 according to the rate laws for the dissociation mechanism are 16.2 ± 2.4 and 15.2 ± 1.2 sec^{-1} at −17°. The correspondence between these values supports the existence of the dissociation mechanism for this system.

The activation energy for this process was determined to be 15.4 ± 0.6 kcal/mole (Figure 1). This activation energy was determined using methylene chloride as a solvent although the concentration study was made in methylcyclohexane. Values obtained in methylcyclohexane averaged 14.5 ± 1.0 kcal/mole but were less reliable owing to interference by the solvent signal.

TABLE III

CALCULATED ENTROPIES OF ACTIVATION

	Solvent	ΔH, kcal/mole	Temp,[a] °K	k_1[b]	$\Delta S^{\ddagger}$, eu
$In(CH_3)_3 \cdot N(CH_3)_3$	Methylcyclohexane	19.4	256	6.7 sec^{-1}	+21
$In(CH_3)_3 \cdot NH(CH_3)_2$	Methylene chloride	14.9	256	15.6 sec^{-1}	+5.3
$In(CH_3)_3 \cdot NH_2(CH_3)$	Methylene chloride	11.1	236	136.4 l. sec^{-1} mole^{-1}	−1.3

[a] Temperature at which $\Delta S^{\ddagger}$ is calculated. [b] k_1 is the experimental rate constant.

TABLE IV

THE CONCENTRATION DEPENDENCE OF THE $In(CH_3)_3 \cdot N(CH_3)_2H$ SYSTEM AT −17°

[In(CH)$_3$)], M	[In(CH$_3$)$_3$·N(CH$_3$)$_2$], M	$1/\tau_A$, sec^{-1}	$1/\tau_{AB}$, sec^{-1}	$(1/\tau_A)/\{[In(CH_3)_3 \cdot NH(CH_3)_2]/[In(CH_3)_3]\}$ sec^{-1}
0.101	0.110	15.4	13.7	14.1
0.075	0.085	18.9	16.2	16.7
0.071	0.012	19.9	19.6	13.9
0.052	0.068	20.9	14.0	15.9
0.091	0.243	40.9	17.5	15.2
			Av 16.2 ± 2.4	Av 15.2 ± 1.2

The dissociation energy of the trimethylindium–dimethylamine adduct has never been determined but on the basis of this work, an upper limit of 15 kcal/mole can be predicted.

The entropy of activation for this process is also reasonable for the dissociation mechanism as seen in Table III.

It should also be mentioned that the rate constants obtained in methylcyclohexane and methylene chloride are quite similar. For example at −20° they are 8.5 and 10.7 sec^{-1}, respectively. These values are within experimental error of one another and imply that this change in solvent has little effect on the mechanism of reaction. More basic solvents interfere with the reaction by competing for the trimethylindium as previously pointed out.[3]

Results of a kinetic study on the trimethylindium–monomethylamine system are shown in Table V. All samples in this system were made with methylene chloride as a solvent owing to the low solubility of the adduct in methylcyclohexane at the desired temperature. Unlike the first two systems studied, $1/\tau_{AB}$ varies with a change in concentration, indicating that a dissociation path is not the applicable mechanism in this system. An alternate mechanism would be one which is bimolecular in nature, such as

$$(CH_3)_3In^* + (CH_3)_3In \cdot NH_2(CH_3) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3In + (CH_3)_3In^* \cdot NH_2(CH_3)$$

For this mechanism, $1/\tau_A = k_1[AB]$ and $1/\tau_{AB} = k_1[A]$. Values for k_1 calculated from these two equations are given in columns 5 and 6 of Table V as 140 ± 40 and 139 ± 22 l. sec^{-1} mole^{-1}, respectively. It might be pointed out that the large standard deviation in these values could easily stem from the difficulty of obtaining highly accurate concentrations for the systems studied.

On the basis of this fit of the experimental data to the kinetic relationships, a bimolecular electrophilic displacement reaction is proposed for the monomethylamine system. The activation energy for this reaction is 11.6 ± 0.1 kcal/mole which is in reasonable agreement with the proposed mechanism since it is doubtful that the dissociation energy of the adduct would be so low. Therefore, a lower energy pathway would have to be used; namely, a bimolecular displacement reaction. This is also borne out by the change in sign of the entropy of activation (Table III) which indicates that a more ordered system is present in the activated complex.

TABLE V

THE CONCENTRATION DEPENDENCE OF THE $In(CH_3)_3 \cdot N(CH_3)H_2$ SYSTEM AT −37.5°

[In(CH$_3$)$_3$], M	[In(CH$_3$)$_3$·NH$_2$(CH$_3$)], M	$1/\tau_A$, sec^{-1}	$1/\tau_{AB}$, sec^{-1}	$(1/\tau_A)/[AB]$, l. sec^{-1} mole^{-1}	$(1/\tau_{AB})/[A]$, l. sec^{-1} mole^{-1}
0.055	0.086	14.4	6.6	168	120
0.057	0.180	21.1	9.6	117	169
0.077	0.029	5.9	12.5	204	162
0.080	0.077	9.5	9.1	123	114
0.091	0.028	3.9	13.1	139	144
0.160	0.089	7.9	20.5	89	128
				Av 140 ± 40	Av 139 ± 22

In conclusion, the exchange reactions in the trimethylindium–amine systems appear to be very similar to the analogous trimethylgallium systems.[2,3] In both cases the trimethylamine and dimethylamine systems proceed by dissociation mechanisms. However, for monomethylamine, when steric bulk around the nitrogen atom is lessened, the reaction shifts to a lower energy bimolecular mechanism. It is thought that for the first two systems, steric crowding is large enough to prevent approach by the second molecule of the Lewis acid.

Furthermore, the studies on the dimethylamine system in methylcyclohexane and methylene chloride solvents indicate that a change in solvent polarity does not result in an increase in the rate of exchange. This implies that the cage effect that Brown discusses for dissociative processes[10] is not operative for this system. If a solvent cage does form, it is unstable with respect to diffusion of the dissociated species.

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