Hydrolysis of the organomagnesium compound with D_2O and mass spectroscopic analysis of the gaseous hydrocarbon generated in this reaction indicated that only monodeuterated ethane had been formed. No evidence was found for a dideuterated product which would be expected from the hydrolysis of ethylenemagnesium. Furthermore, gas chromatographic analysis of the hydrolysis solution showed that the other organic hydrolysis product was ethanol according to the equation

$$C_2H_5MgOC_2H_5 + 2H_2O \longrightarrow C_2H_6 + Mg(OH)_2 + C_2H_5OH$$

The formulation of the volatile organomagnesium compound as ethylmagnesium ethoxide does not conflict with Wiberg's hydrolysis experiments which showed that one mole of ethane is formed per g.-atom of magnesium.

Ethers can be strongly associated with diethylmagnesium; for example, diethylmagnesium dioxanate is reported to have no detectable vapor pressure below 110°.[2] Since in our work, as in Wiberg's, the diethylmagnesium was obtained from ether–dioxane solutions, formation of ethylmagnesium ethoxide can be rationalized as involving interaction of diethylmagnesium with solvate molecules.

Mixtures of ethylmagnesium ethoxide with transition element compounds, *e.g.*, $TiCl_4$, VCl_4, $VOCl_3$, were found to form coordination catalysts for homo- and copolymerizations of α-olefins in inert aliphatic and aromatic hydrocarbons. Such catalysts, however, are less active than standard coordination catalysts formed from the same transition metal compound and alkylaluminum compounds.

[2] W. Strohmeier and F. Seifert, *Chem. Ber.*, **94**, 2356 (1961).

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Proton Magnetic Resonance Spectrum and Molecular Weight of Trimethylindium in Solution

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When trimethylindium was first prepared it was reported[1] that measurements of the freezing-point depression for benzene solutions showed that the compound was tetrameric in solution. This conclusion has been repeatedly quoted and seems still to be widely accepted[2] although at least one piece of conflicting evidence has been available for some time. This is the value of 13.8 kcal./mole for the heat of sublimation.[3] Since the vapor is monomeric[3] this implies that the intermolecular bonds responsible for the "pseudo-tetrameric" structure of the solid[4] can hardly be strong enough to hold together a tetrameric species in solution. In this note we present evidence that trimethylindium actually exists in solution in the monomeric form.

We originally attempted to confirm the tetrameric nature of dissolved trimethylindium by observing the hydrogen nuclear magnetic resonance (n.m.r.) spectrum at low temperatures. An earlier study[5] had shown that at −75° the n.m.r. spectrum of $Al_2(CH_3)_6$ in cyclopentane consisted of two well separated peaks attributable to terminal and to bridging methyl groups, and we expected analogous results for the supposed $In_4(CH_3)_{12}$.

To prepare trimethylindium, dimethylmercury and an excess of indium metal were sealed in a glass tube in the absence of air and heated at 100° for periods of up to 30 days.[1,6] After purification on the vacuum line the product (formed with yields better than 50%) consisted of white crystals whose melting point (88.0 to 88.5°) and vapor pressure (2.5 mm. at 25°) agreed with the values reported earlier.[3]

The n.m.r. spectrum of a saturated solution of trimethylindium in cyclopentane included only one solute peak, 1.56 p.p.m. upfield from the solvent signal. In a more dilute solution the solute peak occurred at 1.52 p.p.m. Since trimethylindium is only sparingly soluble in cyclopentane this small dilution shift was not studied quantitatively. Reducing the temperature produced an upfield shift of the methyl signal and a progressive loss of intensity as the solubility decreased. At −60°, the lowest temperature at which the signal could be detected, the peak was at 1.74 p.p.m. and was still sharp.

With dichloromethane as solvent a similar dependence of the chemical shift on concentration and temperature was found, and it was possible to reduce the temperature to −90° without losing the signal. For a solution containing 5 mole % trimethylindium the solute peak was at 1.55 p.p.m. (cyclopentane internal reference) at room temperature and at 1.83 p.p.m. at −90°. Again the peak remained sharp at the lowest temperature.

In benzene solution at room temperature the solute peak was at 1.70 p.p.m. and *independent* of concentration over the range 1 to 15 mole %. In toluene also the peak was concentration-independent, at 1.72 p.p.m. Lowering the temperature of the toluene solution to −90° produced no shift of the peak position, nor any broadening.

These results suggested that trimethylindium is monomeric in benzene and toluene and perhaps only slightly associated in the nonaromatic solvents. To test this we reinvestigated the apparent molecular weight by vapor pressure studies.

The isopiestic distillation method[7] was usable only if the equilibration was carried out at or below 0°. At higher temperatures the partial pressure of trimethylindium was sufficient to allow it to transfer from bulb to bulb and spoil the experiment. For a solution of 0.4 mole % of trimethylindium in cyclopentane, the ap-

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[1] L. M. Dennis, R. W. Work, and E. G. Rochow, *J. Am. Chem. Soc.*, **56**, 1047 (1934).

[2] G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 152.

[3] A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).

[4] E. L. Amma and R. E. Rundle, *ibid.*, **80**, 4141 (1958).

[5] N. Muller and D. E. Pritchard, *ibid.*, **82**, 248 (1960).

[6] A. L. Otermat, M.S. Thesis, Purdue University, 1962.

[7] R. Signer, *Ann.*, **478**, 246 (1930).

parent molecular weight at 0° was 178 (formula weight 160). Experiments on two separately prepared solutions containing 3 mole % of trimethylindium in dichloromethane yielded results of 168 and 184, also at 0°.

The apparent molecular weight was also determined by measuring the lowering of vapor pressure for solutions of the compound in benzene and in dichloromethane at room temperature. Results from five benzene solutions ranging in concentration from 3 to 24 mole % fell between 175 and 181 and showed no significant trend with changing concentration. The single experiment with dichloromethane was made with a 1.86 mole % solution and yielded an apparent molecular weight of 188.

Probably the chief source of error in these measurements was the procedure used to determine the amount of trimethylindium present in the solutions whose vapor pressures were studied. For each experiment the compound was sublimed into the sample bulb from a storage bulb which was weighed before and after the transfer. We suspect that during transfer some trimethylindium vapor may have condensed in a part of the vacuum line which could not conveniently be warmed, making the actual amount collected in the sample bulb slightly less than the value obtained from the weighings. This would produce artificially *high* values for the apparent molecular weight.

One of the referees suggested that the apparent molecular weight might be too low as a result of reaction of trimethylindium with traces of water adsorbed on glass surfaces. We tried to minimize such decomposition by thoroughly flaming out all parts of the vacuum line for which this was practicable. Moreover we found during preliminary experiments that the reaction with adsorbed water produced a nonvolatile deposit and also that addition of trimethylindium to solvent contaminated with water led to formation of a precipitate. This *insoluble* material was probably polymeric, but may have been $(CH_3)_2InOH$ or $CH_3In(OH)_2$; the latter is formed when excess water is used.[1] The by-product of hydrolysis, methane, would not have affected the measurements because the sample bulb was chilled and opened to the pump after transferring the trimethylindium. To sum up, the reaction with any moisture remaining despite our precautions would have reduced the amount of solute actually present, and this would have led, again, to an apparent molecular weight *larger* than the true value.

We conclude that trimethylindium dissolves as a monomer rather than as a tetramer in benzene, toluene, dichloromethane, and cyclopentane, although the accuracy of our work is too low to exclude a very slight degree of association. Trimethylindium thus behaves like triethyl- and tripropylindium, which were found to be monomeric in benzene solution.[8]

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Absorption Spectra of Calcium–Ammonia Solutions

BY CALVIN HALLADA AND WILLIAM L. JOLLY

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Preliminary work on the absorption spectrum of calcium in liquid ammonia[1] suggested that, at concentrations around 0.02 *M*, calcium yields less than two moles of ammoniated electrons per gram-atom of metal. However, two liquid phases formed during the make-up of some of the solutions, so no definite conclusions could be reached. In a continuing study of calcium–ammonia solutions, we have reached the point where we wish to report some preliminary results on liquid–liquid phase separation and the results of a more careful study of the spectra.

We wished to prepare solutions for spectral studies at concentrations as high as possible while avoiding liquid–liquid phase separation. Therefore we determined the boundary between the one-phase and two-phase regions on the ammonia-rich side of the $Ca-NH_3$ phase diagram. Conductivity measurements indicated that the bronze phase forms at 0.013 ± 0.002 *M* at −64° and at 0.032 ± 0.003 *M* at −45°. Thus we were able to measure the spectra of solutions as concentrated as 0.025 *M* at −45° without danger of phase separation. In earlier work,[1] the solutions were cooled down to about −70° before warming to −65°, at which temperature the initial spectral measurements were made. This precooling procedure did not affect the alkali metal solutions (the second phase appears at concentrations of about 1 *M* at these temperatures in the case of the alkali metals), but some of the calcium solutions undoubtedly underwent phase separation. It is so difficult to get good mixing between the cell windows that even when the temperature was raised to −55 and −45°, it is doubtful that equilibrium was reachieved.

It is fortunate that spectra of single-phase solutions can be obtained at −45° so that direct comparison with the spectra of alkali metal solutions at this temperature can be made.

Experimental

The absorption spectra of eleven calcium–ammonia solutions have been measured between 6,000 and 25,000 Å. at −45°. Spectra of some of the solutions were also obtained at −50° to see if any unusual temperature effects occurred.

Apparatus II of ref. 1 and a Cary Model 14 spectrophotometer were used for all the measurements. The procedures were similar to those used previously. The calcium metal (United Mineral Co., 99.5% pure) was cut, cleaned, and introduced into the side-arm tube of the cell under argon in a dry bag. The calcium was added from the side arm to liquid ammonia in the make-up cell while the latter was immersed in a chlorobenzene slush (−45°).

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