Since both steps take place in the coordination sphere of the metal, the condition for the formation of the dialkylurea is that the alkylformamide formed in the first step is retained on the metal and undergoes a fast nucleophilic attack on the formyl carbon atom by a second molecule of amine. The second step is perhaps the most difficult to interpret. In order to account for the dehydrogenating properties shown by the manganese system it is probably necessary to invoke the intermediate formation of a metal–hydrogen bond. It is hoped that further work which is presently in progress with different organic substrates will help us to understand this particular point.

One of the possible answers to the question of why manganese is capable of yielding almost exclusively dialkylureas, whereas other metal carbonyls show a lower tendency to do so, is that the higher coordination number of manganese and consequently the large number of π-acceptor CO groups bonded to it facilitates the binding of the formamide group in the coordination sphere. For the same kind of reasons, it is believed that the formation of the dialkylureas occurs on the cationic part of the previously mentioned ionic species $[Mn(CO)_{6-n}L_n]^+[Mn(CO)_{5-n}L_n]^-$, which is probably the active catalyst of the carbonylation reaction.

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The Molecular Weights of Trimethylgallium and Triethylgallium in Solution

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Proton magnetic resonance spectroscopy, vapor pressure lowering measurements, and freezing point determinations have been used to show that both trimethylgallium and triethylgallium are monomeric in solutions in benzene or cyclopentane. Additional evidence is also presented to support the conclusion that trimethylindium is not associated in benzene. Earlier reports to the contrary notwithstanding, it now appears that aluminum is the only metal in group III whose saturated trialkyl derivatives are appreciably dimerized in the liquid state through formation of alkyl-bridge bonds.

Introduction

There have been many reports on the tendency of the trialkyl derivatives (R_3M) of the metals of group III to form alkyl-bridged, associated species in solution.[1] When work on these compounds was begun in this laboratory, the available information could be summarized as follows[1,2]: R_3B: monomeric for R = methyl or ethyl. R_3Al: dimeric for R = methyl; higher alkyl derivatives decreasingly associated as steric requirements of R increase. R_3Ga: methyl derivative evaporates with ΔH = 7.8 kcal./mole to give monomeric vapor, but no molecular weight studies have been made on the compound in the liquid state; ethyl derivative also forms monomeric vapor, with ΔH = 10.2 kcal./mole, but is about 70% dimeric in solution in benzene or cyclohexane. R_3In: methyl derivative tetrameric in benzene solution but sublimes with ΔH = 13.8 kcal./mole giving monomeric vapor; ethyl derivative monomeric both in benzene and in vapor phase; propyl derivative monomeric in benzene. R_3Tl: monomeric in benzene solution for R = methyl or ethyl.

Because these findings seemed to fit into no self-consistent pattern we decided to reinvestigate several of these compounds using proton magnetic resonance and other methods to determine the nature of the dissolved species and, if possible, the heats and free energies of association. Our first conclusion,[3] that trimethylindium dissolves as a monomer rather than a tetramer, is further supported by new evidence reported below. In addition we now find that both trimethylgallium and triethylgallium are actually monomeric in solution. It thus appears that aluminum is the only metal of group III whose saturated alkyl derivatives are associated in solution and that the behavior of the trialkyls of the other group III metals is quite regular.

Experimental

Trimethylindium was prepared from indium and dimethylmercury as already reported.[3]

Trimethylgallium was made from gallium tribromide and trimethylaluminum.[4] The details of the preparation have been described elsewhere.[5] After fractionation on the vacuum line, a product with 8.5 mm. vapor pressure at −28° was obtained; the corresponding value from the literature[6] is 8.41 mm. The purity was checked using the n.m.r. spectrum of a 5 mole % solution of the product in cyclopentane, which showed only a single methyl peak 1.48 p.p.m. upfield from the solvent signal. Taken by itself, this does not prove that the product was free from trimethylaluminum, since the methyl signals from the two compounds would probably coalesce as a result of alkyl group ex-

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(1) See G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter III, for a comprehensive review.

(2) W. Strohmeier, K. Huempfner, K. Miltenberger, and F. Seifert, *Z. Elektrochem.*, **63**, 537 (1959).

(3) N. Muller and A. L. Otermat, *Inorg. Chem.*, **2**, 1075 (1963).

(4) L. I. Zakharkin and O. Yu. Okhlobystin, *J. Gen. Chem. USSR*, **31**, 3417 (1961).

(5) A. L. Otermat, Ph.D. Thesis, Purdue University, 1964.

(6) L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, **54**, 1797 (1958).

change.[7] Fortunately there was available a sample of trimethylgallium, prepared from gallium and dimethylmercury, known to be contaminated with dimethylmercury but certainly free of trimethylaluminum. This sample gave two methyl resonances, one at 1.20 p.p.m. due to dimethylmercury, the other at 1.47 p.p.m. due to trimethylgallium. Since trimethylaluminum in cyclopentane produces[8] a peak at 1.79 p.p.m., it follows that at most a few per cent of trimethylaluminum impurity was present in the trimethylgallium sample.

Triethylgallium was prepared by the reaction of gallium tribromide either with triethylaluminum or with diethylzinc.[5,9] The material from the triethylaluminum reaction melted at about $-82°$ (reported[1] m.p. $-82.3°$) and had a vapor pressure of 6 mm. at 25° (calculated value from literature[10] data, 5.9 mm.). The n.m.r. spectrum (see below) agreed closely with earlier reports. Bromine-containing impurities were shown to be absent by hydrolyzing a portion of the product with dilute nitric acid and adding aqueous silver nitrate; this produced no silver bromide precipitate. Although it was concluded that the purity of the product was substantially better than 90%, the possibility of slight contamination with triethylaluminum is not ruled out. For this reason, the alternative preparation using diethylzinc was undertaken. The product had essentially the same properties as that obtained with triethylaluminum, and samples from both preparations yielded identical molecular weight data (see below).

Solvents.—Commercial Spectroquality benzene was fractionated on the vacuum line. Similarly treated commercial cyclopentane gave erratic molecular weight results unless subjected to at least two distillations through a column packed with glass helices, which removed an uncharacterized impurity detectable by vapor chromatography. Both solvents were stored on the vacuum line over calcium hydride and thoroughly degassed before they were used.

N.m.r. Spectra.—Materials were distilled into Pyrex sample tubes sealed onto the vacuum line and carefully flamed to remove all possible moisture. Estimated volumes of solvent and solute were used to derive approximate concentrations. Since the n.m.r. spectra were rather insensitive to dilution, more accurate knowledge of the concentrations was not required. The Varian HR-60 spectrometer was operated at 56.4 Mc./sec. and Varian variable-temperature accessories were used to obtain low-temperature spectra. Chemical shifts were measured and reported with the peak of the cyclopentane solvent as an internal reference signal, the precision being ± 0.02 p.p.m. or better.

Vapor-Pressure-Lowering Determinations.—A simple apparatus was used to measure directly the difference between the vapor pressure over an alkylgallium solution and that over the pure solvent.[5] It consisted of two 25-ml. bulbs connected to the vacuum line through mercury float valves and attached to opposite arms of a mercury manometer. A known weight of alkylgallium was distilled into one bulb with a known volume of solvent, and a comparable quantity of solvent into the other bulb. Both bulbs were surrounded by a common, stirred water bath, and the contents of each were agitated with a magnetic stirrer. A second manometer was used to determine the pressure over the pure solvent. Mercury levels were read to ± 0.05 mm. with a cathetometer, several readings being averaged to obtain the final values.

Before calculating effective molecular weights from the observed pressure differences two corrections were applied. First, the concentration was corrected to allow for the amount of solvent present in the vapor space (0.1 l.) over the solution, as estimated using the ideal gas law. Secondly, since the triethylgallium solute is slightly volatile, the vapor pressure over the solution was corrected by subtracting its contribution, calculated using Raoult's law. The effect of solute vaporization on the concentration of the solution was found to be negligible. The total effect of both corrections on the apparent molecular weight never exceeded fifteen units.

To test the apparatus and procedure, the effective molecular weight of trimethylaluminum in cyclopentane was determined, with results in excellent agreement with reported values.

Freezing Point Depression Determinations.—The most important factor in the design of freezing point apparatus for use with group III metal alkyls is to minimize with the greatest possible care the degree of contamination with water. Hydrolysis of the metal alkyls appears to form polymeric products and to be the principal cause of spurious, excessively high molecular weight values. We used a simple apparatus with the principal advantage that all glass surfaces which came in contact with the solutions could be carefully flamed under vacuum before the start of the experiment, and all materials could be distilled directly into the apparatus from storage bulbs on the vacuum line.

In essence, the apparatus consisted of a sealed test tube 25 mm. in diameter containing a Teflon-coated magnetic stirring pellet and provided with a well for a Beckmann thermometer and a side arm leading to the vacuum line. After flaming and filling the sample chamber, an outer jacket 42 mm. in diameter was mounted around it to ensure a slow and even rate of cooling, and this outer jacket was surrounded by an ice–water mixture.

For each determination, benzene was first introduced alone into the apparatus and its freezing point determined by running several cooling curves. A weighed amount of solute was then added, and from six to ten cooling curves were run. In each case, the liquid became supercooled by about 0.3° before freezing started. The temperature then rose and remained at a plateau for several minutes (5 to 10 for pure benzene, 1 to 5 for solutions). The plateau temperature was taken as the freezing point unless the plateau was very short, in which case the later portion of the cooling curve was extrapolated back until it crossed the initial, steeply falling portion, and the temperature at this point was taken as the freezing point. For some of the solutions, both procedures were used, giving slightly different freezing points, but it was found that the corresponding molecular weight values differed by less than three units.

Data obtained in successive runs with the same sample scattered somewhat in response to minor changes in conditions such as stirring speed, height of the liquid in the external cooling bath, ratio of water to ice in the bath, and so forth. When the molecular weight of phenanthrene was determined as a check on the procedure, the result was 176 (theoretical 178.2) with a mean deviation of 10 molecular weight units. Hence the method should be capable of detecting solute association if the degree of association is more than a few per cent. The molal freezing point depression constant of benzene was taken as 5.12°.

Results

Trimethylindium.—N.m.r. data and vapor pressure lowering results for trimethylindium were reported earlier.[3] To confirm these findings the molecular weight of trimethylindium in benzene was redetermined using the freezing point technique. For 0.0537 g. of trimethylindium in 11.03 g. of solvent the depression was $0.165 \pm 0.01°$, yielding a molecular weight of 151 ± 10 (formula weight 159.86).

Trimethylgallium.—The n.m.r. spectrum of trimethylgallium differs from those of trimethylaluminum and trimethylindium in being virtually unaffected by changes in temperature down to $-100°$ and by changes in concentration. Between 30 and $-100°$ the signal moves upfield by about 0.03 p.p.m. with respect to that from cyclopentane. This is just above the experimental error and comparable with the temperature shift reported recently[11] for cyclohexane. The dilution

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(7) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).

(8) N. Muller and D. E. Pritchard, *ibid.*, **82**, 248 (1960).

(9) J. J. Eisch, *ibid.*, **84**, 3605 (1962).

(10) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941).

(11) J. L. Jungnickel, *Anal. Chem.*, **35**, 1985 (1963).

shift of 0.01 p.p.m. found over a concentration range from 2 to 28 mole % in cyclopentane is also hardly beyond the experimental error. These results suggest that the solute species is monomeric trimethylgallium or, if not, that the degree of association is independent of temperature and concentration in the ranges for which measurements were made.

Freezing point measurements for two benzene solutions of trimethylgallium gave molecular weights of 118 ± 5, very nearly the same as the formula weight, 114.82. The relative volatility of trimethylgallium made it impractical to use the vapor pressure lowering technique.

Triethylgallium.—The n.m.r. spectrum of triethylgallium had been observed at room temperature and consists of an A_3B_2 pattern with reported internal chemical shift values of 0.50 p.p.m.[12] and 0.56 p.p.m.[13] The signals from the protons of the methylene group occur at the higher field.

Since triethylgallium had been reported to be partially associated in dilute solutions at room temperature, it was expected that its n.m.r. spectrum would be quite sensitive to changes in concentration and temperature and that at low temperatures one would observe effects of the freezing out of exchange between bridging and terminal ethyl groups, analogous to the effects seen[14] in the spectrum of triethylaluminum between room temperature and −60°. In contrast to these expectations, we found the following.

A concentrated solution of triethylgallium in cyclopentane at room temperature produced the well-known A_3B_2 pattern, which was analyzed as described by Narasimhan and Rogers.[13] Using their notation, we found $\nu_A = 18.6$, $\nu_1 = 42.8$, and $\nu_2 = 50.2$ c.p.s., yielding an internal chemical shift of 0.50 p.p.m. ν_A was independent of the temperature and concentration, but ν_1 and ν_2 changed *slightly* upon dilution or cooling. Thus, the internal shift for a 4 mole % solution at room temperature was 0.48 p.p.m., and the concentrated solution at −80° gave a value of 0.56 p.p.m. The over-all appearance of the spectrum changed very little between room temperature and −80°, but further cooling (down to −120°) resulted in broadening of all of the signals in a way that suggested that partial solidification of the sample was responsible.

Like the n.m.r. data for trimethylgallium, these results suggest that only one solute species is present to a significant extent under the experimental conditions and that this species is probably not a dimer, though this possibility cannot be ruled out with complete certainty using n.m.r. alone.

To supplement the n.m.r. measurements, the molecular weight of dissolved triethylgallium was reinvestigated using both the vapor pressure lowering and the freezing point depression method. Results for a typical Raoult's law determination, at 24.5°, were as follows.

Amount of triethylgallium: 0.2272 g. or 1.448×10^{-3} mole
Amount of benzene: 1.06 ml. at 20° or 1.19×10^{-2} mole
Vapor pressure of solvent, $P_S{}^0 = 92.87$ mm.
Amount of benzene in vapor space: 4.1×10^{-4} mole
Amount of benzene in solution: 1.15×10^{-2} mole
Concentration of trimethylgallium (assumed monomeric): 11.2 mole %
Total pressure over solution: 83.29 mm.
Partial pressure of triethylgallium over solution: 0.64 mm.
Pressure of benzene over solution, $P_S = 82.65$ mm.

$$\text{Molecular wt.} = \frac{\text{weight of triethylgallium}}{\text{moles of benzene}} \times \frac{P_S}{P_S{}^0 - P_S} = 159$$

Determinations for a total of three benzene solutions, containing between 4 and 12 mole % triethylgallium, gave results of 160 ± 2, within 2% of the formula weight, 156.90. Two of these solutions were made with triethylgallium prepared from diethylzinc, the third with material made from triethylaluminum.

Molecular weight data obtained with cyclopentane as the solvent were at first erratic and gave anomalously high results. However after several repurifications of the solvent a 9 mole % solution also yielded a molecular weight of 161 ± 2 at room temperature. Cooling to 0° changed the apparent molecular weight to 168, but on the basis of the behavior of the earlier samples it seems likely that this reflects a trace of residual impurity in the solvent.

A freezing point depression of 0.699 ± 0.01° was observed for a solution of 0.2355 g. of triethylgallium in 11.23 g. of benzene, leading to a molecular weight of 154 ± 3, about 2% less than the formula weight.

Discussion

According to the data cited in the Introduction, trimethylindium, trimethylgallium, and triethylgallium have very similar, low heats of vaporization and are monomeric in the gaseous phase. If this information had been all that was available, the obvious inference would have been that all three compounds are unassociated in the liquid phase or in solution. The present study shows that this is indeed the case in spite of earlier reports to the contrary. For trimethylindium, most of our evidence was reported previously,[3] and the new results presented here support the same conclusion. Trimethylgallium has never been reported to be associated in solution, but it seemed important to establish definitively that it dissolves as a monomer because the nature of dissolved trimethylgallium has some bearing on that of the triethyl analog. This follows from a comparison of the degrees of dimerization of the R_3Al compounds, which suggests that triethyl derivatives should be less associated than trimethyl derivatives because of steric effects. The monomeric nature of trimethylgallium now appears to be beyond doubt. While this paper was in preparation, results of infrared and Raman spectroscopic studies on trimethylindium and trimethylgallium were published[15] which also indicate that these two compounds are unassociated in solution.

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(12) S. Brownstein, B. C. Smith, G. Ehrlich, and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).

(13) P. T. Narasimhan and M. T. Rogers, *ibid.*, **82**, 5983 (1960).

(14) J. Smidt, M. P. Groenewege, and H. de Vries, *Rec. trav. Chim.*, **81**, 729 (1962).

(15) J. R. Hall, L. A. Woodward, and E. A. V. Ebsworth, *Spectrochim. Acta*, **20**, 1249 (1964).

For triethylgallium the molecular weights found in this study are consistent with the indirect evidence summarized in the preceding paragraph but not with two earlier molecular weight determinations.[2,16] We feel compelled to conclude that these earlier results must be rejected.

The behavior of the saturated trialkyl derivatives of the group III metals now appears much less capricious than it did when this work was begun, since it has been shown that the aluminum derivatives are the only ones which associate in solution. Granted the advantage of using hindsight, the situation is not too difficult to rationalize. It has been proposed[17] that four principal factors govern the stability of dimers held together by alkyl bridges. Association is favored by: (1) a large difference in electronegativity between the metal and carbon; (2) a low value for the energy required to promote an electron from an s to a p orbital in the valence shell of the metal; (3) a large bond energy for a normal, single bond between the metal and carbon; (4) a minimal amount of inner-shell repulsion between two metal atoms separated by an internuclear distance consistent with the geometry of the dimer. The first two of these are particularly unfavorable if the metal is boron. The last two are expected to become increasingly unfavorable as the atomic number of the metal increases, and hence they probably prohibit dimerization for the trialkyls of gallium, indium, and thallium. This leaves the aluminum compounds as the only ones in which the interplay of all four effects allows association by the kind of bridge bonding proposed in ref. 17.

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[16] L. M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, **54**, 182 (1932).

[17] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

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Iron(II) + Iron(III) Isotope Exchange in Dimethyl Sulfoxide

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The isotope exchange reaction between iron(II) and iron(III) in dimethyl sulfoxide has been studied. The reaction is first order with respect to total Fe(II) and to total Fe(III) concentration. The enthalpy and entropy of activation are 9.6 ± 0.6 kcal./mole and -20 ± 2 cal./deg. mole, respectively. The reaction was studied at various perchloric acid concentrations and ionic strengths and over the entire range of water concentrations from zero added water to purely aqueous solutions. At water concentrations less than approximately 0.1–0.2 *M* and at perchloric acid concentrations greater than approximately 7×10^{-6} *M*, the reaction appears to proceed between the hexakis(dimethyl sulfoxido)iron(II) and (III) complexes.

The iron(II) + iron(III) isotope exchange reaction and its catalysis by various anions has been rather extensively studied.[1] The exchange has also been studied in ice-like media,[2] in certain nonaqueous solvents,[3,4] and in nonaqueous solvent–water mixtures.[5] In isopropyl alcohol[4] the exchange rate was at least 10^8 times slower than in water; the effect of water on the exchange rate was not determined. In nitromethane[3] the effect of water was not determined, but the exchange in rigorously purified solvent was extremely slow. In mixtures of methanol, ethanol, 1-propanol, or acetone with water the rate of exchange decreased with decreasing water concentration down to mole fractions of approximately 0.5, as far as the variation was studied.[5] The results, to date, have tended to indicate that the exchange rate is very slow in nonaqueous solvents either because the mechanism of electron transfer changed or because the lower dielectric constants of the nonaqueous solvents resulted in large coulombic repulsion energies on formation of the activated complex. In dimethyl sulfoxide (DMSO) the exchange rate is not particularly slow and the present report describes a study of orders of reaction, effect of water from mole fraction ∼0 to 1, effect of perchloric acid concentration, ionic strength, and temperature in this solvent.

Experimental

Chemicals.—The solvent, DMSO, was obtained either from the Crown Zellerbach Co. or as 99.9% pure Baker Analyzed reagent from the J. T. Baker Chemical Co. Both sources of DMSO were found to give identical results after purification. Purification consisted of a fractional distillation at 2–3 mm. pressure and ∼50°, collection of the center two-thirds of the distillate, and shaking the latter with Alcoa alumina overnight followed by a fractional distillation at the same pressure and temperature as the first distillation with the center one-half of the distillate being retained for use. The purified solvent was stored in a cold room (5°) in a flask fitted with a magnesium perchlorate guard tube to prevent absorption of moisture. The freshly prepared solvent was analyzed for water content with Mallinckrodt Karl Fischer reagent[6] and found to contain approximately 0.015 *M* water.

Perchloric acid solutions in DMSO were prepared by a cation-exchange method. Dowex 50W-X8 cation-exchange resin (50–100 mesh) was converted to the hydrogen form with a 3 *M* HCl

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[1] To list all the references to past work singly would be prodigal of space. A complete set of references can be found in the two review articles (a) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961), and (b) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962), for literature prior to those two dates. Recent publications are (c) W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963); (d) K. Bächmann and K. H. Lieser, *Z. physik. Chem.* (Frankfurt), **36**, 236 (1963); (e) J. C. Sheppard and L. C. Brown; *J. Phys. Chem.*, **67**, 1025 (1963); (f) R. L. S. Willix, *Trans. Faraday Soc.*, **59**, 1315 (1963); (g) S. Fukushima and W. L. Reynolds, *Talanta*, **11**, 283 (1964); (h) J. Menashi, S. Fukushima, C. Foxx, and W. L. Reynolds, *Inorg. Chem.*, **3**, 1242 (1964); (i) A. McAuley and C. H. Brubaker, Jr., *ibid.*, **3**, 273 (1964).

[2] R. A. Horne, *J. Inorg. Nucl. Chem.*, **25**, 1139 (1963).

[3] A. G. Maddock, *Trans. Faraday Soc.*, **55**, 1268 (1959).

[4] N. Sutin, *J. Phys. Chem.*, **64**, 1766 (1960).

[5] R. A. Horne, Ph.D. Thesis, Columbia University, 1955.

[6] J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.