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TRIETHYLGERMYLLITHIUM ASSOCIATION IN SOLUTIONS STUDIED BY THE METHOD OF X-RAY DIFFRACTION IN LIQUIDS

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Summary

X-ray diffraction patterns for Et_3GeLi solutions in benzene, hexane and tetrahydrofuran (THF) are measured and radial distribution functions (RDF's) are calculated. Narrow peaks are detected in the RDF's pertaining to the distances between atoms of coupled Et_3GeLi molecules. This shows directly that these molecules exist in solution in associated forms. The associate structures are different in hydrocarbon and electron-donor solvents. It is found that the nearest neighbour distance between germanium atoms of coupled molecules is 4.5 Å in benzene and hexane and 4.0 Å in THF solutions. Packing of large associates produces the diffraction peak seen in scattering curves of solutions in the low angle region. The associate dimensions (diameters) are estimated from these peak positions as 12.5—14 Å in hydrocarbons and 10 Å in THF.

Introduction

Recent investigations [1] have shown the reactions of Et_3GeM (where M = Li, Na, K) with benzyl chloride in hydrocarbons afford Et_3Ge and benzyl radicals and show appreciable cage effects, which is not typical of free-radical reactions [2]. This is also the case for the reaction of benzyl chloride with butyllithium where the anomalous cage effect is associated with the fact that butyllithium participates in the reaction as a hexamer [3]. No data are available in the literature about the association of germyllithium compounds. However, the ability of lithium atoms in organolithium compounds to form multicenter bonds [4] suggests that the pronounced cage effects in the reactions of germyllithium derivatives also can be attributed to the reduced reactivity of the organogermanium radicals due to the association.

The most direct way to investigate the problem of association of organogermaniumlithium derivatives in solutions is afforded by X-ray diffraction in the liquid state [5—7]. This method allows one to calculate the atomic radial distribution function (RDF) of a liquid from the experimentally determined intensity of the X-ray scattering $I(s)$ (here $s = 4\pi \sin \vartheta/\lambda$, where 2ϑ is the scattering angle and λ is the radiation wavelength). The formula for RDF calculation is

$$4\pi r^2[\rho(r) - \rho_0] = \frac{2r}{\pi} \int_0^\infty si(s)M(s) \sin sr \, ds \, , \tag{1}$$

where

$$i(s) = KI(s) - \sum f^2(s) - I_{\text{incoh}}(s) \, , \tag{2}$$

K is the normalising constant, which scales $I(s)$ to electron units; $I_{\text{incoh}}(s)$ is the incoherent (Compton) scattering intensity; for a binary solution

$$\sum f^2(s) = x_1 \sum_{i=1}^{n_1} f_i^2(s) + x_2 \sum_{i=1}^{n_2} f_i^2(s) \, , \tag{3}$$

$$M(s) = \left[x_1 \sum_{i=1}^{n_1} f_i(s) + x_2 \sum_{i=1}^{n_2} f_i(s) \right]^{-2} \tag{4}$$

with summation for i over atoms in molecules of kind 1 or 2. Here n_1 and n_2 are the numbers of atoms in the solvent and solute molecules respectively; $f_i(s)$ is the atomic scattering amplitude of the ith atom; x_1 and x_2 are the mole fractions of the components; ρ_0 is the average number density of the stoichiometric units $x_1(m_1) \times x_2(m_2)$ where m_1 and m_2 designate chemical formulae of the components. The function $\rho(r)$ gives the density of the number of interatomic distances in the range of $r - r + dr$. The locations of its peaks determine the most probable interatomic distances in the sample, and the areas under the peaks of the function $4\pi r^2 \rho(r)$ are proportional to the coordination numbers. For binary solution,

$$\rho(r) \approx \sum_i^{n_1} \sum_j^{n_1} w_{ij}^{11} \rho_{ij}^{11}(r) + \sum_i^{n_2} \sum_j^{n_2} w_{ij}^{22} \rho_{ij}^{22}(r) + 2 \sum_i^{n_1} \sum_j^{n_2} w_{ij}^{12} \rho_{ij}^{12}(r) \, , \tag{5}$$

where $\rho_{ij}^{kl}(r)$ is the partial radial density distribution of the j-atoms in the l-kind molecules with respect to the i-atoms in the k-kind molecules (k, $l = 1, 2$), and the weighting factors are

$$w_{ij}^{kl} = x_k z_i z_j \Bigg/ \left[x_1 \sum_i^{n_1} z_i + x_2 \sum_i^{n_2} z_i \right]^2 \, , \tag{6}$$

here z_i is the number of electrons in the i-kind atom.

The above method has been applied in the present work to investigate Et_3GeLi solutions. This method can be used to investigate the associates, owing to two basic factors. Firstly, if there are stable Et_3GeLi complexes in a solution, the RDF must have peaks conforming to the interatomic distances in these aggregates. These peaks must be narrower than those of intermolecular distances for weakly coupled molecules, and therefore more pronounced. Secondly, as seen from eq. 6, the contributions to the RDF from the interatomic distances, involving heavy atoms (Ge), are much higher than that from the other ones. This enhances still further the sensitivity of the method to Et_3GeLi associates in solution, because the distances between germanium atoms give the main contribution to the RDF.

Experimental technique and calculations

The solutions of Et_3GeLi (concentration of 2—4 mol/l) were produced by the method reported in ref. 8. For the X-ray scattering measurements the samples were in a thin-walled (0.01 mm) glass capillary of about 1 mm diameter placed on the axis of a DRON-2 X-ray diffractometer. The scattering intensities were measured using monochromatic Mo-K_α radiation which was obtained by a bent and ground crystal monochromator (LiF) mounted in the diffracted beam. This geometry allowed us to eliminate the fluorescent radiation of the germanium atoms. The scattering angle ranges were $2.5^\circ \leqslant 2\vartheta \leqslant 60^\circ$ for solutions and up to 90—100° for pure solvents. The times to accumulate 10^4 counts were measured at each discrete angle.

The procedure for treating the experimental scattering curves, including RDF calculations, is described in ref. 9. The scattering amplitudes of CH, CH_2 and CH_3 groups were taken into account by the method reported in ref. 10. This means that these groups are seen in RDF as a hole as "quasi-atoms", and not as separate C and H atoms. We did not know precise mole fractions of the components in solution. Therefore, the values of x_2 were selected using the diffraction data themselves. When calculating the RDFs, the correct values of x_2 give false minimum low-frequency oscillations in the curves $si(s)M(s)$, which hence give only small false peaks in the RDF's at r values lower than the minimum interatomic distances in the samples [11]. The false termination peaks and those associated with random errors in the experimental intensity curves were eliminated from the final RDFs by the procedure reported in ref. 12 (eq. 6 and 7). Four terms corresponding to the first four sharp peaks in the RDFs of the solutions were taken into account in these formulae, instead of the two terms used in ref. 12.

Results and discussion

The RDFs of benzene (solvent) and Et_3GeLi solutions in benzene are shown in Fig. 1. On the basis of the known bond lengths, the peaks observed in the RDF in the region 1.4—3.0 Å can be attributed to the intramolecular interatomic distances. The nearest neighbour distances between the CH groups in a benzene molecule and those between CH_2 and CH_3 groups in a Et_3GeLi molecule contribute to the first peak. The second peak at $r \approx 2$ Å is basically associated with the nearest neighbour Ge—CH_2 distances. In this case the value of r is close to the Ge—C bond length 1.98 ± 0.03 Å in a tetramethylgermanium molecule [13]. The location of the third peak at $r \approx 2.9$—3.0 Å is determined by the Ge—CH_3 distances. These distances are close to those expected, provided the

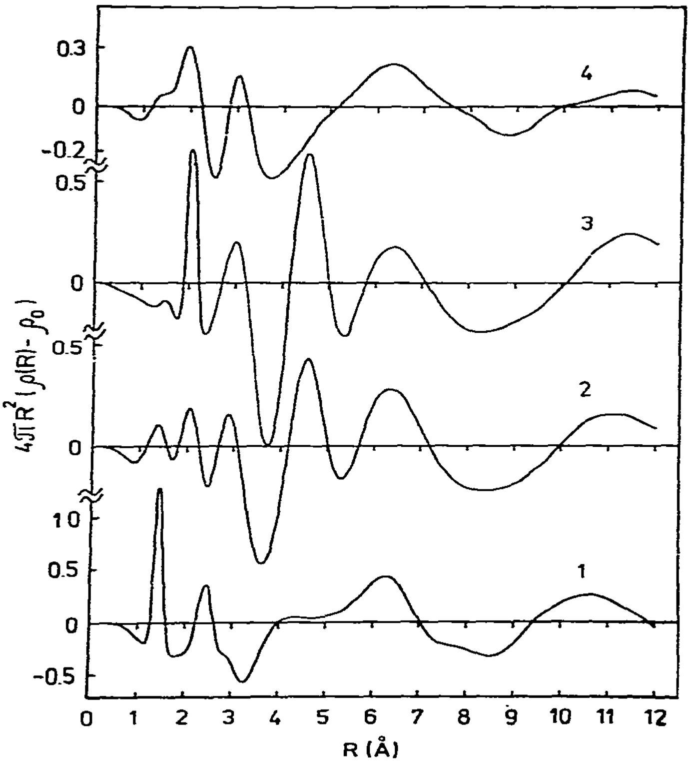

Fig. 1. Radial distribution functions for: 1, benzene; 2 and 3, Et_3GeLi solution in benzene, $x_2 = 0.21$ and 0.45, respectively; 4, Et_3GeH solution in benzene, $x_2 = 0.31$.

lengths of the Ge—CH_2 and CH_3—CH_2 bonds are assumed to be 2.0 and 1.54 Å, respectively, and the angle between these bonds is tetrahedral.

The intense and rather narrow peak in the RFD's at $r = 4.5$—4.6 Å is of greatest interest for the problem under consideration. The intramolecular interatomic distances cannot have such values in the solutions studied. Therefore, the observed peak may refer only to the interatomic distances in Et_3GeLi associates. The comparison of the RDFs for Et_3GeLi and Et_3GeH (curve 4) solutions affords unambiguous evidence for this statement. The latter compound has a molecular structure similar to that of Et_3GeLi; however, it is undoubtedly not associated since it contains a hydrogen atom instead of lithium one, which ensures the binding of the molecules in the associate. Indeed, there is no peak at $r = 4.5$ Å in curve 4, only those from the intramolecular distances, like in Et_3GeLi solutions. The broad intermolecular distance distributions observed are characteristic of molecules not coupled by strong interactions. This is, e.g., the case for benzene RDF (curve 1) at $r > 3$ Å.

The main contribution to the area of the peak discussed here must be made by the distance of the types Ge—Ge, Ge—CH_2 or Ge—CH_3, as can be readily seen from eq. 5 and 6. Their weighting factors in the RDF are: $w(\text{Ge—Ge}) = 0.121$ and $w(\text{Ge—CH}_2) \approx w(\text{Ge—CH}_3) = 0.03$ (for $x_2 = 0.45$, curve 3). Though the latter value is less than the former one, the distances of the type Ge—CH_2 or Ge—CH_3 must be more numerous in associate, than Ge—Ge ones. Therefore, their contribution to the peak area can be of comparable magnitude. The weighting factors for the distances not involving germanium atoms are much less than those given above; for example, $w(CH_2—CH_2) = 0.008$ ($x_2 = 0.45$). Hence, their contributions to the peak are negligible. The location of the RDF maximum discussed is determined, most likely, by the maximum in the distribution of distances between neighbouring germanium atoms in the associates. Firstly, the weighting factor in the RDF for these distances is the largest. Secondly, the superposition of the Ge—CH_2 distance distributions cannot shift the peak considerably. In any model of the complex, with a given mean nearest neighbour Ge—Ge distance, there should be a number of distances between a Ge atom and different CH_2 and CH_3 groups. Therefore, the resulting Ge—CH_2 and Ge—CH_3 distance distribution would be much broader than that of Ge—Ge. Thus, the mean nearest neighbour Ge—Ge distance in the associate is approximately 4.5 Å, as follows from the position of the peak maximum.

Similar results have been obtained for Et_3GeLi solutions in hexane. The RDF for the most concentrated solution investigated is shown in Fig. 2. The peak in the RDF corresponding to interatomic distances in the associates is at the same position and its intensity and width are close to those observed in the benzene solutions. This means that the nature of association and the structure of the Et_3GeLi associates are the same in these solvents.

The influence of electron-donor solvents on the association is of great interest. As is known from literature [4], molecules of such solvents can form complexes with organolithium compounds. Tetrahydrofuran is an example of such a solvent. The RDFs for THF and Et_3GeLi in THF solution are shown in Fig. 3. The peak of the interatomic distances in the associates is observed (curve 2) at $r = 4$ Å, i.e. is displaced by 0.5 Å and is much narrower compared to the analogous peak in hydrocarbon solutions. If one assumes the location of the peak maximum to be determined, as before, by the mean nearest neighbour distance

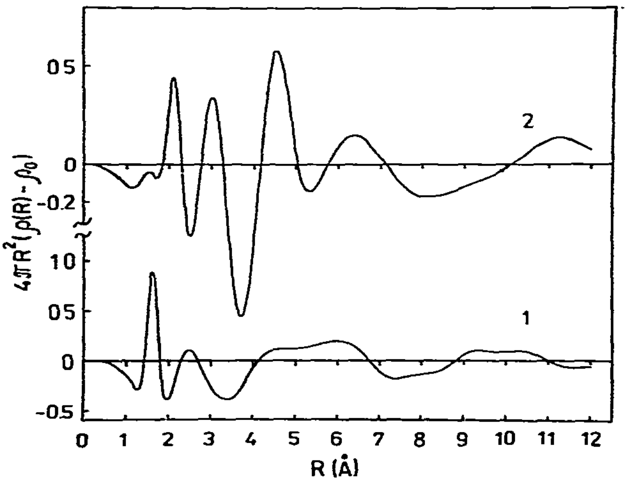

Fig. 2. The same as in Fig. 1 for: 1, hexane, 2, Et_3GeLi solution in hexane ($x_2 = 0.31$).

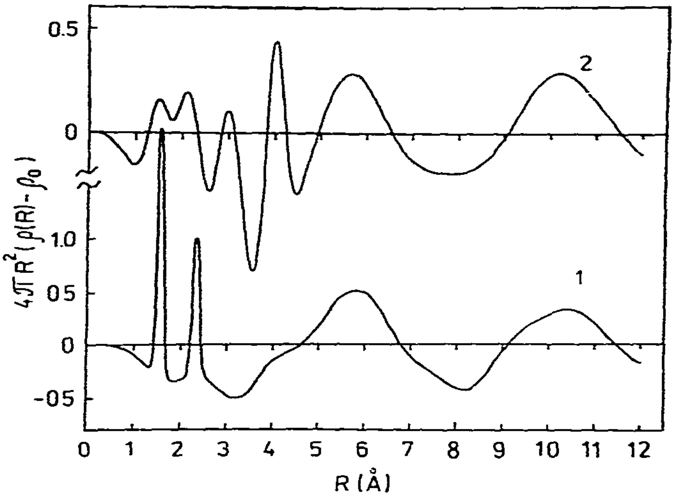

Fig. 3. The same as in Fig. 1 for: 1, THF; 2, Et_3GeLi solution in THF (x_2 = 0.15).

between the germanium atoms, then a reduction of this distance indicates that the packing of the Et_3GeLi molecules in the associate is more compact. It is possible that the associates contain solvent molecules together with Et_3GeLi ones and that the character of the bonding in the complex differs from that in hydrocarbons. In particular, the narrower width of the peak at 4 Å, i.e. the smaller distribution of interatomic distances, can result from stronger coupling between molecules in the associate. One more possible reason for the sharpening of the peak is that this peak, which is the superposition of different interatomic separation distributions, is contributed to by distances which are closer in value. In any case the considerable differences in the behaviour of this peak show that the associate structure in THF differs greatly from that in hydrocarbons.

Besides the RDF's, information about the associate dimensions can be obtained from analysis of the scattering intensity curves in the region of their main diffraction peaks. Such curves are shown in Fig. 4. In the case of Et_3GeLi solutions a new scattering maximum appears to the left of the peak observed in the pure solvent. Comparison with the diffraction curve of Et_3GeH solution (curve 4) having no such peak demonstrates that this peak results from Et_3GeLi association. The simplest explanation for this peak is as follows. The associates of Et_3GeLi molecules are of nearly spherical form and the diffraction by the packing of these spheres produces the peak observed. The location of the peak in the small angle region (small s values) proves that the diameter of the spheres appreciably exceeds the dimensions of the Et_3GeLi molecule. The value of s_{max}, that is the location of the peak maximum, allows one to estimate the associate diameter R from the formula $R = 7.73/s_{max}$ [7]. s_{max} = 0.55—0.62 Å^{-1} * in benzene and hexane solutions, which corresponds to R = 12.5—14 Å. As seen from Fig. 4, the small angle peak is displaced towards higher s values (s_{max} =

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* s_{max} decreases slightly with decreasing concentration of the solution, since the exact location of the maximum is affected by the packing density of the particles, as well as their size.

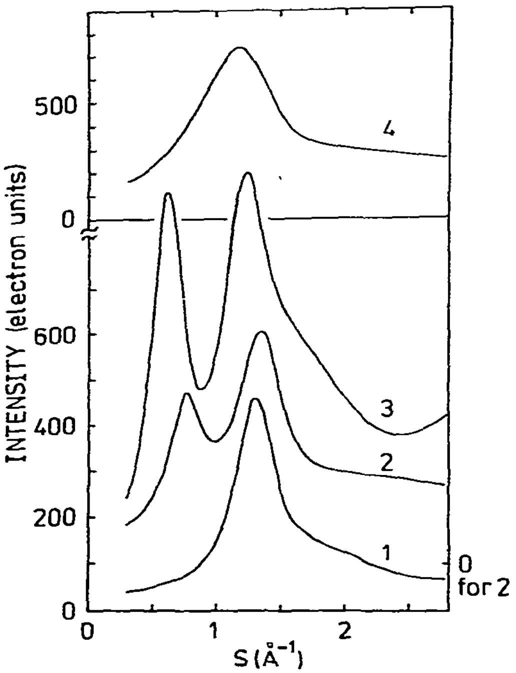

Fig. 4. The normalized to electron units scattering intensities for: 1, benzene; 2, Et_3GeLi solution in THF (x_2 = 0.15); 3, Et_3GeLi solution in benzene (x_2 = 0.45); 4, Et_3GeH solution in benzene (x_2 = 0.31).

0.77 Å^{-1}) in THF solution, i.e. the associate diameter (R = 10 Å) is less than that in benzene or hexane. This is more evidence for the fact that the associates have different natures in electron-donor and neutral solvents.

Conclusion

Data obtained by various methods give some information about the association of organolithium compounds in solutions [4]. It should be emphasized once again that the basic merit of the diffraction method is the possibility of observing direct structural effects caused by the aggregation of molecules. This feature of the method ensures no ambiguity in the evidence obtained for the existence of Et_3GeLi associates in solutions, and also the difference in their structures in electron-donor and neutral solvents. Further quantitative analysis of the data obtained in this work could allow the determination of the associate structure. Work in this direction is in progress.

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