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Investigation of Gamma-Ray Induced Polymer Formation of the Carboranes

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INTRODUCTION

During the past year the overall problem of the investigation of the radiation induced polymerization in organo substituted derivatives of 1,2-dicarba-closo-dodecaborane-(11), o-carborane, has been continued. In view of the shift in emphasis of this program in the future to the study of the Radiation Chemistry of Plastic Crystals, see Renewal Proposal, the work on co-polymerization and cross-linking of these compounds with monomers forming organic polymers was discontinued. The primary emphasis was placed on the completion of the study of radiation induced polymerization of the pure carborane type compounds. Also, the research effort and thus the results reported for this period were reduced by a time gap of several months between the departure of one postdoctoral research associate, Dr. R. M. Thibault, and the hiring of his replacement, Dr. M. A. Mathur. This effect was compounded by Dr. Mathur's automobile accident shortly after he started work, which prevented his working for several months.

In an attempt to draw definitive conclusions concerning the polymerization of these compounds, three projects were carried out during this period: theoretical calculations of charge transfer in these compounds and their radicals; and two experimental studies of o-carborane and 1-phenyl-o-carborane as test cases for the tentative conclusions previously proposed. A fourth project, which involved both theoretical calculations and experimental measurements was completed in order to provide basic information on the plastic crystalline solid state of these compounds. These four projects are discussed individually below under the Scientific Scope.

SCIENTIFIC SCOPE

A. INDO Calculations of Charge Transfer.

Background - Evidence reported previously [1--6] supports a free-radical mechanism for an addition polymerization of 1-alkenyl-o-carboranes leading to two different oligomeric products. One product is a polystyrene-like polymer with pendant o-carborane groups on a polyethylene backbone, polymer A. A second product is a polymer which incorporates the o-carborane cage in the polymer backbone, i.e., a "string of beads" structure, polymer B. The formation of polymer A has been fairly well established from ESR studies [7] of the radicals involved and from analysis of the polymer material [1--6]. The initiation and propagation steps for the formation of polymer B, however, are unknown, but must involve the formation of a cage radical [7].

Project Work - In order that a cage carborane radical be formed as postulated previously in the formation of polymer B, there must be an increase in electron density of the carborane cage. Thus, this project was undertaken to establish whether or not charge transfer occurred between the alkenyl side chain and the cage. Since the aim of this calculation was limited to obtaining reasonable correlations with experimental data, it falls short of initiating a new search for better algorithms for approximate molecular orbital methods, or of impractically large ab initio calculations for large heteroborane systems.

The calculations were performed with the INDO (Intermediate Neglect of Differential Overlap) all-valence electron SCF (Self-Consistent Field) program developed by Pople and coworkers [8] and available as the Dobosh-Pople computer program CNINDO [9]. The calculations were performed

on The University of Mississippi DEC 1077 digital computer. The cartesian coordinates for the o-carborane atoms were derived from the atom positions in the crystal structure of Potenza and Lipscomb [10]. A specially written computer program [11] checked the substituent coordinates for chemically unreasonable approaches to the cage atoms or to each other, and rejected absurd geometries. The program also allowed rotation of the substituent atoms about any C-C bond, and thus allowed INDO checks on the substituent conformation dependence. In addition to the calculations on the alkenyl substituted carboranes, an open shell-spin doublet INDO calculation for the free radical derived from 1-vinyl-o-carborane by removal of a hydrogen atom was carried out. This work together with the tabulated mathematical results are shown in the attached journal preprint.

Significance - The results of this calculation show an increase in electron density of the cage at the expense of the side chain, i.e., electron density is "pumped" from the side chain into the carborane cage. This result then supports the formation and stabilization of a cage radical postulated previously. Thus, it appears that the formation of polymer B may be attributed, both on experimental and theoretical grounds, to partial stabilization of the carborane cage free radical due to the increase in electron density of the cage as a result of substitution of an organic side chain. The open shell-spin doublet INDO calculation for the free radical derived from removing a hydrogen atom from the side chain carbon α to the cage indicates that the net charge transfer from substituent to cage is preserved for the free radical as well as the neutral molecule.

B. Dipole Moments and Plastic Crystallinity.

Background - In the course of our previous work on gamma-ray induced polymerization of organo substituted carboranes [1-4], it was found that the nature of the solid state, i.e., plastic crystallinity, played an important role in the radiolysis reactions [5,6]. In order to better understand these reactions, it was felt that additional information on the nature of the monomers was required. As a result the present study was carried out on several organo-substituted carboranes to determine if there was a relationship between their dipole moments and their plastic crystallinity.

Project Work - The determination of the dipole moments of several organo substituted carboranes of interest to the radiation induced polymerization studies were carried out experimentally utilizing the method of Guggenheim [12] and Smith [13]. The calculated values of the dipole moments and their orientation were determined using the INDO all-electron SCF program of Pople and co-workers [8] discussed previously in section A above.

The INDO dipole moments are larger than the experimental values by a factor of about two. However, of greater importance than the actual values of the dipole moments is the orientation of the dipole moment vector, which is from CTR, the arithmetic mean of non-hydrogen atoms of the o-carborane cage (positive charge end) to approximately the mid-point between the C1 and C2 atoms of the cage (negative end). The substitution of various organic groups at the C1 cage position does not change the y- and z- direction cosines of the dipole moment. However, a small shift in the x- direction cosine was observed. A

check on the vinyl substituent conformation dependence of the INDO results showed that the dipole moment was not affected by rotating the vinyl group around the VCl-Cl bond. Details of the experimental and INDO calculations are presented in the attached journal preprint.

Significance - No correlation was found between the experimental (or the INDO) dipole moments and the mesophase transition temperatures. Also there was no obvious difference in dipole moments for those organo-substituted carboranes that are plastic crystalline and those that are not. Since these results are based on the single-molecule charge distributions, where direct Coulomb forces are dominant, the concept that plastic crystallinity is essentially a dispersion energy effect is reinforced.

Although the results of this project were partially negative in the sense of furthering our understanding of the plastic crystallinity of the monomers under study, the experimentally determined dipole moments of these organo substituted carboranes will be very useful in the investigation of the electro-optical properties of these compounds proposed for the next contract period.

C. o-Carborane Radiolysis.

Background - In the study of the radiation induced polymerization of organo-substituted carboranes two types of polymers have been observed. One product is a polystyrene-like polymer with pendant o-carborane groups on a polyethylene backbone, polymer A. A second product is a polymer which incorporates the o-carborane cage in the polymer backbone, i.e., a "string of beads" structure, polymer B. We have postulated previously from experimental evidence [7] and on

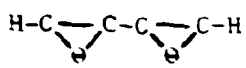
theoretical grounds (section A above) that formation of polymer B involves electron charge transfer from the organic side chain to the carborane cage. As a result it is of interest to test this conclusion by examining the polymer formed from o-carborane, itself, where there is no opportunity for charge transfer to occur. Also the examination of the radiation chemistry of this compound is important since it is the parent compound of the series of organo-substituted compounds that have been under study for some time.

Project Work - The radiolysis of o-carborane in the solid state was carried out on 200 mg samples of the material sealed under vacuum which had been carefully purified to remove especially CO_2 and water [14]. The samples were irradiated at 31°C either in the University's Co-60 Source or electron accelerator as a function of total dose up to 100 MRads. The detectable products of the reaction were three gases and three solids.

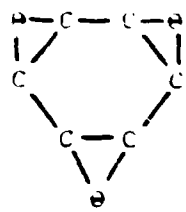
Gas chromatographic (GC) analysis of the gaseous products using a Porapak-Q column showed them to be hydrogen, methane and acetylene. Hydrogen production was found to decrease from a G-value of 2.5 to 0.7 as a function of total dose in the range 2 to 14 MRads and then to remain constant at G_{H_2} = 0.70 to total doses of 100 MRads. Methane production was found to vary in a similar manner from G-values of 1.0 to 0.2 in the range of 2 to 14 MRads and then remaining constant at G_{CH_4} = 0.2 for higher total doses. The third gas, acetylene, on the other hand did not show an initial sharp decrease in G-value with total dose but rather decreased linearly from 0.5 at 2 MRads to 0.4 at 20 MRads.

The previously used [14] techniques for separation of the solid products from the unreacted monomer were not found to be effective in this system. Separation was achieved not only of the monomer from the products, but also of the products from each other by the use of Analytical Liquid Chromatography (ALC) using a poragel-100 column and methylene chloride as the mobile phase. The unreacted o-carborane was identified by column retention time and mass spectral analysis. The consumption of o-carborane was found to decrease rapidly from a G-value of 265 at 2 MRads to a $G_{(-m)}$ = 31 at 14 MRads at which point it remained constant for all higher total doses examined. The high G-value for disappearance of the monomer is, of course, indicative of a chain process being involved in the radiolysis. The consumption of o-carborane over the entire total dose range was zero ordered and independent of total dose within experimental error, i.e., only approximately 32% of the o-carborane was consumed in the radiolysis reactions at any given total dose in the range of 2 MRads to 100 MRads.

The first of the three products observed in the ALC analysis was identified by mass spectral analysis as an adduct trimer of o-carborane which must have a cyclic six-member carbon ring to account for the observed mass spectra. The structure of the trimer is shown in Figure 1. The absence of higher molecular weight oligomers both in the ALC and in the mass spectra of the whole radiolysate, which have been observed in radiolysis of organo-substituted-o-carboranes [1--6], may be attributed to the formation of this cyclic trimer which effectively terminates chain propagation.



DIMER



TRIMER

$\Theta = B_{10}H_{10}$

Figure 1

The second product, observed in the largest quantity, in the ALC separation was shown by mass spectral analysis to be the adduct dimer of o-carborane. Since only one dimer was found in the ALC of the radiolysate, whereas in the case of the radiolysis of 1-Allyl-o-Carborane seven dimers were separated [4] by ALC, it must be concluded that only one type of linkage between the carborane cages is possible. By inference from the structure of the trimer, this linkage must be of the polyethylene type through the carbon atoms of the cage or what has been termed previously as giving rise to polymer A. The structure of the dimer is shown in Figure 1. The linkage which would give rise to polymer B could not lead to the observed cyclic trimer, but only to a linear oligomer, which was not found in detectable quantities. The proton-nmr of the mixed dimer-trimer shows a decrease in the cage C-H band intensity compared to o-carborane in qualitative agreement with the above conclusions as to the structure of the dimer and trimer. Sufficient amounts of the dimer-trimer mixture are not produced in the radiolysis to allow separate or quantitative nmr analysis to be made.

The third product separated by ALC was again shown by mass spectral analysis to be the higher boron hydride icosaborane-16, $B_{20}H_{16}$ [15]. Since the methane and acetylene observed in the radiolysis must come from breakdown of the cage, it appears that the $B_{10}H_{10}$ fragment from this process must dimerize to give the observed $B_{20}H_{16}$ product, as well as contributing to the production of hydrogen. GC analysis of the mixed dimer-trimer-icosaborane-16 combination on an SE-30 column using acetone as the solvent for these solids allowed quantitative determination of the G-value of $B_{20}H_{16}$ as a function of total dose (the dimer and trimer are not passed by this column). The production of icosaborane-16 drops from a G-value of 0.26 at 2 MRads to 0.1 at 20 MRads and is essentially constant with dose thereafter up to 100 MRads. This decrease in the formation of icosaborane-16 parallels the decrease observed for hydrogen, methane and acetylene.

There are several experiments currently underway to complete this work on the study of the o-carborane system. One of these is the synthesis of icosaborane-16 [16] to allow a positive confirmation to be made of the GC retention time on the SE-30 column used for G-value determination of this product. Also an investigation is underway to determine the effect of the methane, acetylene and icosaborane-16 products in limiting the consumption of o-carborane to about 32%, regardless of the total dose given the sample. These experiments involve the effect of removal of the gaseous products during radiolysis as well as the addition of these gases and icosaborane-16 prior to radiolysis.

Significance - Although the o-carborane in the solid state at 31°C is not a true plastic crystal, it is a disordered solid [17] and as such will have molecular mobility greater than that of a true crystalline

solid but less than that of a plastic crystal. This fact needs to be kept in mind when comparing this system to the organo-substituted carborane systems previously studied [1--7], [18]. This decreased mobility in the o-carborane system may be one of the more important factors affecting the large decrease in yield of oligomeric products in this system compared to the organo-substituted carborane systems.

One of the striking conclusions found in this study is that only one type of oligomer linkage is found, i.e., the polyethylene type with pendant carboranyl groups. The theoretical work in Section A above predicted that this should be the case when there is no group attached to the carborane which can pump electron density into the cage. Thus, the experimental work on the o-carborane system provides additional support for this theoretical predication of the necessity of charge transfer to the cage in order to form the B type of polymer.

In our previous work on organo-substituted carboranes, there was no indication of degradation of the carborane cage, i.e., formation of boron hydride decomposition products. The o-carborane system does show some decomposition of the cage as evidenced by the formation of methane, acetylene and icosaborane-16. However, the amount of cage decomposition is extremely small (0.1% at 2 MRads increasing to 0.5% at 20 MRads, based on the mass balance of carbon in the system) compared to the amount of o-carborane consumed that forms dimer and trimer. Thus, it can be concluded that degradation of the carborane cage in radiolytic polymerization is negligibly small under the most favorable conditions, i.e., the absence of substituent groups on the carborane.

Another important consideration in this study is that, although the disappearance of the monomer, $G_{(-m)}$, is large, indicative of a chain process (the $G_{(-m)}$ of o-carborane is comparable in value to that observed for the organo-substituted carboranes), it is the only carborane system to show consumption of the monomer to be independent of the total dose and to be zero ordered. This unusual behavior tends to indicate that some mechanism is present which efficiently stabilizes the o-carborane cage after about 32% of the o-carborane has reacted either by degradation or by oligomerization. The reasons for this behavior may be due to the catalytic nature of one of the products to reform o-carborane or to some other mechanism. This point is currently under investigation.

The last point of significance in this study of the o-carborane system is the formation of a cyclic trimer. Thus far in the study of the organo-substituted carboranes there has been no evidence of cyclic products. This may simply be due to the fact that in the organo-substituted carboranes the smallest ring compounds that could be formed by the linkage of polymer A would be an 8 or 10 member ring. Also, in the case of polymer B, the ring size would have to be very large in the organo-substituted carborane oligomers. However, in the case of the o-carborane the formation of a six-member carbon ring should be a highly favored process.

D. Radiolysis of 1-Phenyl-o-Carborane.

Background - As indicated in the previous sections of this report, A and C, the type of polymer formed, A or B and/or a combination of the two, appears to be dependent on the ability of the organic side chain to transfer electron density to the carborane cage. In the case of o-carborane, there was no possibility of electron charge transfer to

the cage. On the other hand, 1-phenyl-o-carborane is a system in which the phenyl group, an electron rich group, is conjugated with the electron deficient carborane cage and therefore is capable of charge transfer to the carborane cage. Thus, as expected,only polymer A was formed with the o-carborane system, whereas the formation of polymer B would be expected to compete favorably with the formation of polymer A in the 1-phenyl-o-carborane system. In order to test this assumption, the study of the gamma-ray radiolysis of 1-phenyl-o-carborane was undertaken.

Project Work - Since 1-phenyl-o-carborane (POC) was not commercially available, it was synthesized from commercially obtained decaborane-14 by first forming the $B_{10}H_{12}\cdot 2CH_3CN$ [19]. This intermediate was then reacted with $C_6H_5C{\equiv}CH$ to form 1-phenyl-o-carborane [20,21]. The POC was purified by recrystallization from n-pentane and finally by vacuum sublimation. The purified product melting point and spectral data agreed with the literature values [20,21]. Also gas chromatography (GC) and analytical liquid chromatography (ALC) analysis showed it to be chromatographically pure.

Before beginning the investigation of the radiolysis of 1-phenyl-o-carborane system in the solid state, the material was analyzed to determine whether it was a true plastic crystal as previously reported [17] or a disordered solid like o-carborane (OC). Differential Scanning Calorimetry (DSC) of the material showed four phase transitions. These phase transitions together with their entropy changes are given in Table 1. The entropy change for the melting point transition at +65°C is almost twice the limit

Table 1

DSC of 1-Phenyl-o-Carborane

Temperature, °C	ΔH, cal/gram	ΔS, e.u.
-32	0.64	0.58
-13	0.77	0.65
- 2	1.34	1.09
+19	0.80	0.60
+65	13.91	9.05

of 5 e.u. usually accepted for plastic crystals [22]. Also the sum of the ΔS's for the four phase transitions below the melting point of 2.92 e.u. is less than that of the melting point. In terms of the accepted criteria for plastic crystallinity [22], 1-phenyl-o-carborane is not a true plastic crystal. However, the presence of the four phase transitions below the melting point are indicative of a disordered crystal with the highest state of disorder occurring in the ambient temperature range.

The radiolysis of POC was carried out on approximately 200 mg samples of the material sealed under vacuum. The samples were irradiated at 31°C in the University's Co-60 source as a function of total dose up to 26 MRads. The detectable products of the radiolysis were three gases and three or possibly four solids.

GC analysis of the gaseous products using a Porpak-Q column showed them to be hydrogen, methane and acetylene. The production of all three gases decreased rapidly in the range of 2 to 6 MRads total dose, becoming

almost constant with total dose above 16 MRads. The G-values for these three gases at 2 MRads and 26 MRads are shown in Table 2 below. The formation of the gaseous products methane and acetylene indicated

Table 2

G-values for Gaseous Products

Gas	POC 2 MRads	OC 2 MRads	POC 26 MRads	OC 26 MRads
Hydrogen	1.4	2.5	0.2	0.7
Methane	0.7	1.0	0.03	0.2
Acetylene	0.06	0.5	0.006	0.4

decomposition of the POC during radiolysis. However, it is impossible to determine from the present data whether these gases are being formed from decomposition of the phenyl substituent or from the decomposition of the cage itself. As a result, it is not possible to set up an unambiguous carbon mass balance for this system as was done in the case of o-carborane, *Section C above*. However, comparison of the G-values in the POC system with those of OC, Table 2, for the lowest and highest doses indicates that the decomposition side reaction is smaller than in the o-carborane system. It can be roughly estimated from this comparison that in the POC radiolysis, decomposition will range from less than 0.1% at the lowest dose to 0.05% at the highest dose. Thus, in the POC system, decomposition is a very negligible side reaction.

In the analysis of the solid radiolysate, it was found that the unreacted POC could be separated from the products by vacuum sublimation. ALC analysis showed the sublimate to be pure unreacted 1-phenyl-o-carborane. The residue from the sublimation was found by ALC to contain a trace of POC and three additional peaks, one very strong and two weak, using the refractive index detector. As a result, at the present time, there are definitely three and possibly four solid products of the radiolysis. The identification and yield determination of these products is currently being investigated.

The determination of the amount of unreacted POC, which has thus far only been identified by ALC retention time, allowed determination of the $G_{(-m)}$ as a function of total dose. The G-values for disappearance of the monomer decreased rapidly from 29.5 at 2 MRads to 2.8 at 16 MRads and then decreased very slowly to 1.5 at 26 MRads. The high $G_{(-m)}$ at the low doses indicates a chain reaction is initially involved in the radiolysis. The sharp break in the $G_{(-m)}$ as a function of total dose at about 16 MRads suggests a change in mechanism of the radiolysis reaction to a process not involving a chain reaction. This point is also currently under study.

Significance - Although the investigation of the radiolysis of the 1-phenyl-o-carborane is in the preliminary stages and no definitive conclusions can be drawn at this time, there are several significant results which have emerged concerning this system. Unlike the previously studied alkenyl-substituted carboranes [1--6], the solid state of POC has been shown to be a disordered crystal like that of OC [17] rather than a true plastic crystal. As a result, in terms of mobility

in the solid state, the POC system can be compared with the OC system more readily than with the alkenyl-substituted carboranes. The nature then of the solid state of POC has an advantage in assessing experimentally the effect of substituent charge transfer to the cage in terms of the type of oligomer formed by it compared to that formed by OC. On the other hand, the nature of the solid state of POC has a disadvantage in that the restricted mobility should decrease the amount and chain length of the oligomer formed by radiolysis compared to that of the alkenyl-substituted carboranes.

The second result obtained from this study is that the amount of degradation in the radiolysis, as evidenced by the formation of methane and acetylene, is even less than that in the OC system, where it was shown to be negligible compared to oligomer formation. The increased stability of POC to radiolytic degradation is probably due to stabilization of the system by charge transfer from the substituent phenyl group to the carborane cage.

The third fact to arise from this work is that the consumption of POC, except in the earliest stages, is not a chain process as it was in the o-carborane and alkenyl-substituted carborane systems. Also the amount of monomer consumed is an order of magnitude less in the POC system compared to the OC system, neglecting the very small side reaction leading to degradation in both cases. This last difference between the two systems may be attributed to the absence of an efficient chain process in the POC system. The reasons for the absence of a chain reaction in POC, which is unique among the substituted carboranes studied, will require further investigation.

It should be stressed that the conclusion discussed above with regard to the radiolysis of POC are tentative at this time. These conclusions may be revised as the investigation proceeds and additional data are developed. Also, the primary reason for the study of this system has yet not been answered, i.e., the role of charge transfer from the substituent to the cage on the type of oligomer linkage formed.

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A. Journal Articles.

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D. Meeting Papers.

1. T. J. Klingen and J. R. Wright, "Investigation of the Radiolysis of Cyclohexane in the Plastic Crystalline State", 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Alabama, November 1972.

2. M. A. Mathur and T. J. Klingen. "Investigation of the Gamma-Ray Radiolysis of o-Carborane", Southeastern-Southwestern Regional Meeting of the American Chemical Society, Memphis, Tennessee, October 1975.

3. T. J. Klingen, J. H. Kindsvater and R. M. Metzger, "INDO Calculations of Dipole Moments and Charge Densities of a Series of Organo-Substituted Carboranes", Southeastern-Southwestern Regional Meeting of the American Chemical Society, Memphis, Tennessee, October 1975.

PERSONNEL

A. Contract Supported.

1. Dr. T. J. Klingen, Principal Investigator, part-time.

2. Dr. M A. Mathur, Postdoctoral Research Associate, full-time.

B. Graduate School Supported.

1. Mr. D. V. Smith, student technician, part-time (March through May 1975).

2. Mr. W. S. Howard, student technician, part-time (June 1975 to present).

C. Unsupported.

1. Dr. R. M. Metzger, Assistant Professor of Chemistry, contributed his expertise in computer programing.