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ANNUAL PROGRESS REPORT TO THE

UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Contract Number AT-(40-1)-3781

The Radiation Chemistry of Plastic Crystals

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Department of Chemistry
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Report Period: November 1, 1975 to October 31, 1976

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SYNTHESIS AND PLASTIC CRYSTALLINITY OF THE ADAMANTANE SERIES

Background-- In order to expand the scope of the overall project to include compounds other than those of the carborane series, work was started this year on the derivatives of the adamantane series. This series of compounds was chosen for a number of reasons. First of all adamantane itself is a classic plastic crystal, although one without a dipole moment. Secondly, there are many stable derivatives of adamantane which are commercially available or which can be synthesized by proven literature methods [1--10]. Thirdly, the derivatives of adamantane, in addition to having a high probability of being plastic crystalline, also would have reasonably high dipole moments. Lastly, the study of a homologous series of compounds such as the adamantane derivatives may provide some insights into the nature of the plastic crystalline state itself.

Project Work-- Of the derivatives of adamantane reported in this section, several were obtained commercially and the remainder prepared using the cited literature methods [1--10]. All of the compounds obtained from either source were purified until the proper melting points were obtained. Before use the purity was checked chromatographically. These compounds were then examined to determine the temperature range and transition entropies of the plastic crystalline state. This phase of the investigation was carried out using Differential Scanning Calorimetry (DSC).

It has been shown that the plastic crystalline state exhibits at least one and usually two or more reversible endotherms below the isotropic melting point of the compound [11]. The presence of these sharp reproducible endotherms provides evidence for the liquid-like motion in the solid state of the compound, as well as evidence that the material is not amorphous. Also DSC provides the phase transition entropies. This is important since a plastic crystal should have an isotropic melting entropy of less than 5 e.u. with the majority of the entropy release being associated with the lower mesophase transitions [12]. The DSC of the compounds investigated in this section are shown in Table 1, in terms of the mesophase transition temperatures and their associated entropies.

Table 1

DSC of Adamantane Derivatives

Compound	t, °C	ΔS, e.u.	Type of Solid
1-Flouro-Adamantane	-217	[illegible]	Crystalline
1-Chloro-Adamantane	[illegible] -13 [illegible] -117 -163	[illegible] [illegible] [illegible] [illegible] 1.40	Plastic Crystalline
1-Bromo-Adamantane	[illegible] -77 -116	0.24 [illegible] [illegible]	Plastic Crystalline
1-Nitro-Adamantane	-13 -156	[illegible] 1.0	Plastic Crystalline
1-Amino-Adamantane	-11 -192 -219	[illegible] 2.71 3.80	Plastic Crystalline
1-COOH-Adamantane	-18 -61 -175	1.[illegible] 13.3 [illegible]	Disordered Crystalline Solid
1-methyl ester-Adamantane	-40	13.[illegible]	Crystalline
1-OH-Adamantane	-86 -246	6.[illegible] 11.0	Disordered Crystalline Solid
1-Phenyl-Adamantane	-52 -79	2.11 10.3	Disordered Crystalline Solid
1-Phospha-2,8,9-Trioxa-Adamantane	-46 -26 -202	3.26 2.06 2.12	Plastic Crystalline
9-Thiabicyclo-[3.3.1] Nonane	-31 -170	2.34 5.26	Disordered Crystalline Solid
9-Thiabicucle-[3.3.1] Nonane dioxide	-112 -338	10.[illegible] 3.7	Plastic Crystalline

For the establishment of plastic crystallinity in compounds, it is not sufficient only to show liquid-like character in the solid phase, but also that crystalline order, at least in terms of short range forces, has been retained. This can best be demonstrated by X-ray powder diffraction studies of the mesophases of the compounds. The X-ray powder diffraction photographs of all the adamantane derivatives shown in Table 1 have been obtained at room temperature and all show crystalline order. Those compounds for which the X-ray data has been indexed are shown in Table 2. The indexing of this X-ray data was done using the computer program of Roof [13] modified for the DEC-10™ system.

It is anticipated that using the variable temperature X-ray camera developed in this laboratory [14], the lattice structures will be determined for each mesophase of the compounds shown to be plastic crystalline, similiar to that previously determined for the carborane series [15].

Significance-- Of the twelve adamantane derivatives examined thus far, 50% have been found to be true plastic crystals and 33% to be disordered solids; i.e., only two of the twelve compounds are true crystalline solids at all temperatures below the melting point. These results indicate that the adamantane series is one in which a large number of plastic crystalline derivatives exist and thus it is well suited to the overall purpose of this study. The synthesis of other adamantane derivatives is currently underway to expand the number of available plastic crystals in this series.

On the basis of the compounds examined thus far in this study, it was noted that none of the compounds capable of hydrogen bonding was found to be a true plastic crystal. This suggest then that hydrogen bonding may be one of the factors which inhibits free rotation in the solid state. However, on the basis of the small amount of data obtained so far, this must be considered a tentative conclusion, subject to further study.

Table 2

X-Ray Powder Diffraction Data

Compound	a	b	c	α	β	γ	Lattice
1-fluoro-adamantane	9.58	9.58	7.42	---	---	---	Hexagonal (rhombohedral)
1-bromo-adamantane	6.20	7.13	10.67	84.08	75.15	82.15	Triclinic
1-phenyl-adamantane	13.50	15.30	14.60	---	---	87	Monoclinic
1-phospha-2,6,9-trioxadamantane	6.14	6.43	10.95	89.05	82.38	69.93	Triclinic
9-thiabicyclo-[3.3.1.]-nonane	11.79	6.73	6.75	90	122	90	Monoclinic

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ELECTRO-OPTICAL STUDIES

Background-- Since organo-substituted carboranes, in the plastic crystalline solid state, have been shown to be materials well suited for high speed electro-optical switching [1--3] which may find application in devices generating high energy radiation, it is of some practical importance to determine whether or not radiation-generated chemical impurities affect the electro-optical behavior of plastic crystals. If they do affect the electro-optical properties of plastic crystals, then the nature and level of chemical impurities as a function of radiation dose and electro-optical degradation need to be determined.

Project Work-- In order to carry out meaningful electro-optical measurements on plastic crystals a d.c. Kerr cell type of system was set-up [4]. A block diagram of this system is shown in Figure 1. The light from a 450 watt Xenon lamp was passed through a variable wavelength monochrometer. The light emerging from the monochrometer was polarized at 45° to the electric field of the Kerr cell using a Nichol polarizer. This polarized light then passed into a temperature controlled chamber containing the Kerr cell. The temperature inside the chamber can be varied from -40 to +150°C. Kerr cells of varying electro-gap and light path length were made of copper which was gold plated and with windows of UV grade fused silica. D.C. potentials applied to the Kerr cell were variable from 0 to 5000 volts. The light emerging from the Kerr cell then passed through a second Nichol polarizer, which was oriented perpendicular to the applied electric field, and into an IP-28A photomultiplier detector. The photomultiplier output was read on a digital voltmeter, and in the cases where a range of wavelengths was scanned, it was also plotted as a function of wavelength using a strip chart recorder. Also all entrance and exit light ports in this system are of UV grade fused silica.

This system has only recently become operational due to delays by the manufacturers in delivery of several of the components for this system. Also additional time was consumed in attempting to

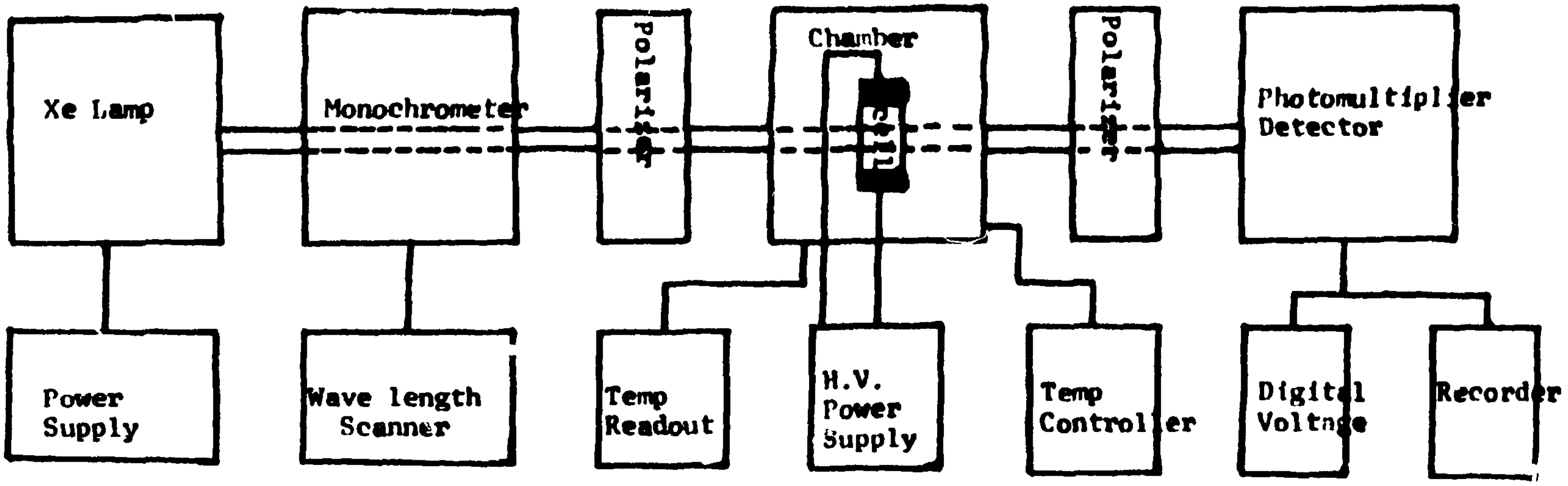
Xe Lamp
Monochrometer
Polarizer
Chamber
Cell
Polarizer
Photomultiplier Detector
Power Supply
Wave length Scanner
Temp Readout
H.V. Power Supply
Temp Controller
Digital Voltage
Recorder

Figure 1

use a He-Ne Laser as the light source for this system. As a result of this initial testing, it became evident that a variable wavelength laser source would probably be the best light source for use in this system. However, in view of the high costs involved, the Xenon light source and monochrometer arrangement was chosen as the best compromise.

The initial studies carried out on this system were on unirradiated samples and were designed primarily to establish optimum operating parameters, such as electro-gap, cell path length, method of sample preparation and so forth, relative to nitro-benzene as a standard [1,5]. The results of these studies are shown in Table 1, for nitrobenzene, 1-vinyl-o-carborane (VOC) and 1-ethyl-o-carborane (EOC). The last column in this Table, which essentially is a measure of the amount of rotation of the polarized light in the presence of the electric field compared to the absence of the electric field, shows that not only the path length of the Kerr cell but also the method of sample preparation, i.e., mechanical packing of the plastic crystal into the Kerr cell versus melting it into the cell followed by cooling to room temperature, has a great effect on the results. The most consistent results (data shown in Table 1 is the average of a number of runs) obtained thus far are for the Kerr cell having an electro-gap of 0.7 cm and a path length of 0.6 cm when the sample is prepared from the melt. Under these conditions VOC showed an electro-optical effect ten times larger than nitrobenzene, whereas EOC showed an effect which was about twice that of nitrobenzene. It should also be noted that the applied voltages given in Table 1 produced the maximum Kerr effect for the particular material. This fact was determined by measuring the change in photomultiplier output, relative degree of rotation of the light beam, as a function of voltage applied to the Kerr cell at several wavelengths for each compound. In the case of all three systems, it was found that above a threshold voltage, the photomultiplier output varied linearly with applied voltage until a plateau was reached. The onset and plateau voltages for the Kerr effect on these compounds are shown in Table 2.

Table 1

Electro-Optical Parameters

Compound	λ max nm	Electro-Gap cm	Cell Path Length, cm	Applied Voltage VDC	Temp. C	Change in PM Output, μv
ØNO$_2$	440	0.3	0.3	1,000	24	+ 10
	440	0.3	0.6	1,000	24	+ 70
	450	0.2	1.2	1,000	24	+ 500
VOC	430	0.3	0.3	4,000	24	+ 150[a]
	420	0.3	0.6	4,000	24	+ 80[b]
	415	0.3	0.6	4,000	24	+ 700[a]
	400	0.2	1.2	4,000	24	+ 80[b]
EOC	400	0.3	0.3	4,000	24	+ 20[b]
	400	0.3	0.6	4,000	24	+ 50[b]
	400	0.3	0.6	4,000	24	+ 150[a]
	400	0.3	0.6	4,000	40	-1,000[c]
	370	0.2	1.2	4,000	24	+ 250[b]

[a] Samples prepared by melting the compound into the cell and slowly cooling to room temperature.

[b] Samples prepared by mechanical compression of the compound into the cell.

[c] Sample in the liquid state.

Table 2

Kerr Effect as a Function of Voltage

Compound	Cell Size	Onset Voltage	Plateau Voltage
ϕNO_2	0.3 x 0.6 cm	500	1,000
VOC	0.3 x 0.6 cm	500	2,800
EOC	0.3 x 0.6 cm	2,400	3,000

In Table 2 above, it can be seen that the onset voltage of VOC and EOC are quite different under the same conditions. Since the dipole moments of these compounds are comparable, 4.56 and 4.96 Debyes respectively, it may be that the difference in onset voltage may be related to the rotational barrier of the plastic crystalline state. In this regard, the test of temperature control of the Kerr cell chamber gave results, shown in Table 1 for EOC, which showed a very large rotation of light for EOC in the liquid phase at 40°C compared to the plastic crystalline phase at 24°C, i.e., -1,000 at 40°C compared to 150 at 24°C, indicating a difference in the energy barrier for ordering in the two different phases. The reversal of direction of rotation of the light in the liquid phase compared to the plastic crystalline phase, as indicated by the sign, is not understood at this time and will require further investigation.

Significance-- Although only the set-up and initial testing of this system have been completed thus far, i.e., no irradiated samples have been examined, several interesting results have emerged:

1. the temperature study of EOC has shown the electro-optical method to be very sensitive to phase changes;
2. the variation of rotation with applied voltage suggest the method may provide information on the rotational energy barriers in plastic crystalline mesophases when measured as a function of temperature;

3. the magnitude of the Kerr effect in the plastic crystalline solids does not, on the basis of initial work, appear to be dependent on the magnitude of the dipole moment of the compound, although a dipole moment may be necessary to observe the effect; and

4. the magnitude of the electro-optical effect is much larger for the plastic crystalline carboranes than for nitrobenzene, which is considered to have a very high effect.

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RADIOLYSIS OF 1-PHENYL-o-CARBORANE

Background-- It has been predicted on theoretical grounds that electron transfer from a substituent to the carborane cage affects the type of polymer formed during radiolysis [1]. Also it has been shown in the case of o-carborane, a disordered solid, that only an oligomer of the polyethylene type of linkage with pendant carborane groups formed. [2]. The absences of a competing type of polymer involving the carborane cage was attributed to the lack of charge transfer due to the absence of a substituent group. 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 $B_{10}H_{12}\cdot 2CH_3CN$ [3]. This intermediate was then reacted with $C_6H_5C \equiv CH$ to form 1-phenyl-o-carborane [4,5]. 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 [4,5]. Also gas chromatography (GC) and analytical liquid chromatography (ALC) analysis showed it to be chromatographically pure.

Before beginning the investigation of the radiolysis of POC in the solid state, the material was analyzed to determine whether it was a true plastic crystal as previously reported [6] 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 transitions at +65°C is almost twice the limit of 5 e.u. usually accepted for plastic crystals [7]. Also the sum of the Δ S'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 [7], POC 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 occuring in the ambient temperature range.

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

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 four gases and three solids.

GC analysis of the gaseous products using a Porpak-Q column showed three of the gases to be hydrogen, methane and ethylene. 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 6 and 18 MRads are shown in Table 2 below. The formation of the gaseous products, methane and ethylene, indicated decomposition of the POC during radiolysis.

Table 2

G-values for Gaseous Products

Gas	POC 6 MRads	OC* 6 MRads	POC 18 MRads	OC* 18 MRads
Hydrogen	0.8	1.5	0.2	0.6
Methane	0.1	0.2	0.07	0.2
Ethylene	0.06	0.3	0.02	0.4

* Data taken from Ref. 2.

A small amount of a fourth gas was identified on an SE-30 GC column as being benzene with a G-value of 0.4 at a dose of 19.8 MRads. However, it is impossible to determine from the present data, except for benzene, 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 OC [2]. However, comparison of the G-values in the POC system with those of OC, Table 2, for the high and low doses indicates that the decomposition side reaction is smaller than in the OC system. It can be roughly estimated from this comparison that in the POC radiolysis, decomposition will be less than half that observed for the OC, where it was negligible. 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 POC. The residue from the sublimation was found by ALC to contain a trace of POC and three additional peaks. Since the Poragel-100 column used separates the material on the basis of molecular weight, a series of compounds of known molecular weight (between 76 and 805 amu) were analyzed on this ALC column under the same conditions as the radiolysate. These standard materials showed a linear relationship of retention time with molecular weight [8] giving rise to the following equation,

$$\text{Retention time} \quad -5.409 \times 10^{-3} \cdot \text{Mol. Wt.} + 10.156692.$$

Using this equation the molecular weights of the three radiolysis products of POC were, within 3%, the molecular weights of the POC adduct dimer, trimer and tetramer.

Mass spectral analysis of the radiolysate after ALC separation to confirm the above assignments showed the oligomeric products to be either non-volatile even at 260 °C in the mass spectrometer, or that they formed multiple charged ions, since the analysis failed to show any mass numbers above 308 with the maximum intensity at 219 amu.

The proton nmr of the irradiated solid products were essentially the same as the unirradiated POC. However, the peak areas due to the cage carbon protons and the peak area due to the phenyl protons were considerably decreased in the irradiated samples compared to the unirradiated sample of POC, as shown in Table 3. Also the ratio of the phenyl proton area to the cage carbon proton area remained, within experimental error, essentially constant for all samples as shown in Table 3.

The determination of the amount of unreacted POC, which was identified by ALC retention time and confirmed by mass spectral analysis, allowed determination of the $G_{(-m)}$ as a function of the total dose. These results are shown in Table 4.

Table 3

Proton nmr of POC as a Function of Dose*

Dose, MRads	Cage C-H $\delta = 3.88$ ppm	Phenyl-H $\delta = 7.37$ ppm	Phenyl-H/Cage C-H Ratio
0.00	112	473	4.22
1.00	86	381	4.43
4.00	102	324	3.18
5.00	83	407	4.90
7.00	90	389	4.32
13.00	85	407	4.79

* Peak areas normalized to 100 mg of POC in CCl_4 as the solvent with TMS as the standard.

Table 4

Disappearance of POC

Dose, MRads	$G_{(-m)}$
0.25	510
0.50	101
0.74	32.2
1.00	23.1
4.00	0.6
5.00	0.8
7.00	0.5
13.00	0.4
29.20	0.5

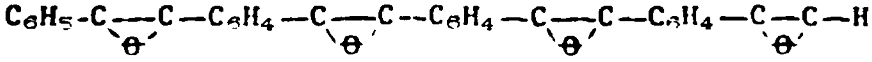
The sharp break in the $G_{(-m)}$ data between one and four MRads suggests a change in mechanism, with the reactior involving a chain process at the lower doses and a non-chain process occurring for doses greater than 4 MRads.

Significance-- Unlike the previously studied alkenyl-substituted carboranes [9-15], the solid state of POC has been shown to be a disordered crystal like that of OC [2] 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 restricted mobility of the disordered solid state, however, resulted in a decreased yield and a decrease in chain length of the oligomer formed by the radiolysis. This restricted mobility may also affect the nature of the oligomer formed, i.e., the polymerization may be "topotatic" [16,17].

The second result obtained from this study is that the amount of degradation in the radiolysis, as evidenced by the formation of hydrogen, methane, ethylene, and benzene, 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 [1].

A 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 magntiude less in the POC system compared to the OC system, even if the very small side reaction leading to degradation is neglected. This last difference between the two systems may be attributed to the absence of an efficient chain process in the POC system at the higher doses due to the stabilizing effect of the phenyl ring system.

The fourth conclusion that arises from this work is the structure of the oligomeric products. The molecular weight determination of the oligomeric products indicate that they are the adduct dimer, trimer, and tetramer of POC. Of the various oligomer structures possible, only one agrees with the nmr data shown in Table 3 above, i.e., a decrease in both cage carbon proton signal and phenyl proton signal with the ratio of the two signals remaining essentially constant with radiation dose. This structure must be of the linear polyethylene type thru the phenyl ring with pendenant carborane groups, as is shown in Figure 1 below



$$C_6H_5{-}\underset{\theta}{C{-}C}{-}C_6H_4{-}\underset{\theta}{C{-}C}{-}C_6H_4{-}\underset{\theta}{C{-}C}{-}C_6H_4{-}\underset{\theta}{C{-}C}{-}H$$

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

Figure 1

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CO-POLYMERIZATION OF THE CARBORANES

Background-- In the course of completing the polymerization studies on the organo-substituted carboranes, one of the final studies to be undertaken was the co-polymerization of those compounds with a commercially important monomer, of which there are a large number. Somewhat arbitrarily the monomer chosen was 1,3-dicyanobenzene (IPN) which has application in the formation of superpolyamide fibers [1-3], has with m-xylylenediamine resinous coating properties [4] and is in general a very versatile monomer when combined with other compounds to form co-polymers [5-7]. The co-polymerization studies reported here were limited to *o*-Carborane (OC) and 1-vinyl-*o*-carborane (VOC). These studies were, however, carried out using both thermal energy and gamma-rays to initiate the reactions in the solid state.

Project Work-- a. Thermal Initiation-- An equimolar quantity of IPN and OC, which had been shown to be chromatographically pure, was prepared by simple mixing. Observation of the capillary melting of this mixture indicated that the IPN melted near its normal melting point followed by solvation of the OC. The DSC of this equimolar mixture showed a large reaction endo-therm at 254°C, well above the melting point of either IPN or OC. This endotherm was similar to those described by Yang and Steinberg [8]. Using the equations developed by Yang and Steinberg [8] a computer program was written to calculate the activation energy for the IPN-OC reaction endotherm. The results of this calculation indicate an activation energy for the thermal reaction at 254°C of 32.2 kcl/mole.

Gram quantities of this equimolar mixture of IPN-OC were sealed under vacuum in pyrex and reacted at 254°C for 17 to 26 hours. After heating the material was sublimed to remove any unreacted material. The residue was found to have a DSC pattern completely different from either IPN or OC. The sublimate was shown by infrared spectra to be pure IPN.

ALC of this residue showed only two peaks of molecular weight greater than IPN. Using the standardization curve of retention time versus molecular weight, (see previous section on 1-phenyl-o-carborane radiolysis) the molecular weighs were determined from ALC to be 390 and 630. These values are within 2% of the values for the trimer and pentamer of IPN itself. Mass spectral analysis of the reaction residue is shown in Table 1.

Table 1

Mass Spectra of IPN-OC Thermal Reaction Products*

Mass Number	Relative Intensity	Assignment
102	13.0	ϕCN
128	100.0	IPN
144	0.2	OC
256	2.2	$(IPN)_2$
384	42.0	$(IPN)_3$

* Inlet Temperature 250°C

This data in Table 1 clearly shows the presence of the trimer of IPN. The absence of the pentamer may be due to either its being non-volatile in the mass spectrometer or to its break-down in the mass spectrometer. The latter would account for the presence of the small amount of dimer and the large amount of monomer observed. However, it will also be noted in this table that only a trace amount of OC was observed.

Attempts to carry out a similiar reaction involving equimolar quantities of IPN-VOC resulted in the sublimation of the VOC, m.p. = 70°C, out of the reaction mixture. As a result of this, analysis of the mixture after heating indicated that no reaction had occured. This problem is being investigated further at this time.

b. Gamma-Ray Initiation-- In the case of gamma-ray initiation at ambient temperature (31°C), where solution of one compound in the other is not possible, equimolar quantities of IPN-OC and IPN-VOC were dissolved in xylene and then the solvent was removed to provide an intimate mixture of the two components. Prior to use, these mixtures were examined by nmr and GC to determine the complete removal of the xylene solvent.

Samples of IPN-OC and IPN-VOC prepared in this manner were sealed under vacuum and irrdaiated at ambient temperature in the Co-60 source to total doses of 10 MRads. GC analysis of the gases produced during the radiolysis of both IPN-OC and IPN-VOC showed five peaks of which three have been thus far identified as hydrogen, methane, and ethylene. The solid material from the IPN-OC and the IPN-VOC radiolyses were sublimed under vacuum. In all cases the sublimates were determined from infrared spectral data to be pure unreacted IPN. ALC analysis of both IPN-OC and IPN-VOC sublimation residues showed the presence in each case of only one peak of higher molecular weight than the starting materials. At the present time, the results of mass spectral analysis of the solid residues of IPN-OC and IPN-VOC are being awaited before proceeding further with this investigation.

Significance-- Several results of the thermally initiated reaction appear to have significance even though the original objective of co-polymerization of IPN with the carboranes was not achieved. The heating of pure IPN does not result in polymerization of IPN; however, in the presence of o-carborane IPN does polymerize to an adduct oligomer with a chain length of at least five units. Obviously from the data developed thus far, o-carborane plays a catalytic role in the thermal reaction. The nature of this role, as well as the structure of the IPN oligomer formed, still has to be elucidated.

The second significant point of this work is the demonstration of the applicability of the work of Yang and Steinberg [8] on solid-gas phase reactions to thermal liquid phase reactions for the determination of the reaction activation energy. In the case of the IPN oligomerization catalyzed by OC, the activation energy was shown to be 32.2 kcal/mole.

In the case of the gamma-ray induced co-polymerization of IPN with OC and VOC, it has been shown that a reaction has occured which leads to a higher molecular weight product. This higher molecular weight material, which must contain both IPN and OC in combination, has physical properties resembling those of a soft organic plastic. Definitive conclusions will have to await the results of the work currently being conducted on these systems.

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CONTRACT PUBLICATIONS

A. Journal Articles.

1. T. J. Klingen and M. Howard, Jr., "The Radiolysis of *o*-Carborane in Benzene Solution", *Rad. Res.*, **40**, 484, (1969).

2. J. R. Wright and T. J. Klingen, "Investigation of Gamma-Ray Induced Polymer Formation in the Carboranes. I. Separation and Structural Identification of the Polymer Formed from 1-Vinyl-*o*-Carborane", *J. Inorg. Nucl. Chem.*, **32**, 2853 (1970).

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B. Patents.

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C. Dissertations.

1. John R. Wright, "The Radiation Chemistry of Icosahedral Carborane Condensed Phases: 1-Vinyl- and 1-Isopropenyl-*o*-Carborane", Ph.D. Dissertation, The University of Mississippi, August, 1971.

2. David R. Hepburn, Jr., "Polymerization of 1-Allyl-*o*-Carborane Induced by Ionizing Radiation", Ph.D. Dissertation, The University of Mississippi, August, 1974.

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. E. L. Rowe, student technician, part-time (January through May, 1976).
2. Mr. B. J. Johnson, Jr., student technician, part-time (June, 1976 to the present).

C. Unsupported.

1. Dr. N. E. Heimer, Associate Professor of Chemistry, contributed his expertise in organic synthesis and X-ray analysis.