ORO-3781-1.0



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## Investigation of Gamma-Ray Induced Polymer Formation of the Carboranes

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## PURPOSE

The research reported herein is concerned with the investigation of the radiation chemistry of o-carborane [1,2-dicarba-closo-dodecaborane (11)] and its 1-alkyl and 1-alkenyl derivatives. The principle purpose of the research is to establish optimum conditions for radiation-induced polymerization of such compounds. Properties and structures of polymeric products, identities and yields of minor products, and reaction mechanisms are being determined.

## INTRODUCTION

During the current report period, the understanding of the chemistry of reaction intermediates in the radiation-induced reactions of the carboranes has advanced considerably. Previous work discussed in ORO-3781-9 and earlier reports has demonstrated the possibility of efficient solid-state radiation-initiated polymerization of 1-alkenyl-o-carboranes. Many mechanistic parameters have been obtained, especially for 1-vinyl-o-carborane. Some evidence has been obtained which indicates that the plastic crystallinity of the solid phase of such substances as 1-vinyl-o-carborane and cyclohexane has an important influence upon their radiation chemistry.

Two projects have been continued from the last report period (1) a study of EPR spectra of γ-irradiated solid carboranes at 77°K

has continued and has grown to include EPR measurements of γ-irradiated alkane glass solvents containing carborane solutes (2) A study of radiation-initiated polymerization of pure 1-allyl-o-carborane has been partially completed. Preliminary results are compared in this report with those from previous studies of 1-vinyl-o-carborane.

In addition, several new projects have been completed. A thorough study of the radiolysis of cyclohexane solutions of four carboranes has provided an explanation of the radiation chemistry of carborane anions and radicals in solution. Such information will be useful in proposed studies of solution co-polymerization and some results such as the estimated electron scavenging ability of the carborane cage will be of general interest to radiation chemists. Results obtained on the radiolysis of 1-vinyl-o-carborane in various other solvents is also discussed. In addition, the ultraviolet absorption spectra of a series of carboranes has been re-examined leading to a refined understanding of cage-substituent interaction.

Only preliminary results are available for two other new studies. The first of these is a study of the optical absorption spectra of γ-irradiated alkane glasses containing carborane solutes. Results from this work will be correlated with the EPR study and will facilitate interpretation of results from proposed pulse radiolysis studies. The second topic is the co-polymerization of 1-alkenyl-o-carboranes with other vinyl monomers. Preliminary results are presented for solutions of styrene and 1-vinyl-o-carborane.

Two other phases of this research program which have been scheduled are (1) a study of reaction mechanisms and kinetics in model plastic crystalline matrices and (2) a study by pulse radiolysis

of reaction intermediates in carborane radiation chemistry. Owing to delays in equipment delivery and preoccupation with other aspects of this research, these studies have been postponed until the later half of the current funding period.

## EXPERIMENTAL

New or improved experimental equipment and techniques used in this project will be described in detail in this section. Other equipment and techniques have been explained in previous reports, (ORO-3781-8 and ORO-3781-9).

Materials-- o-Carborane (Alfa Inorganics), 1-vinyl-o-carborane (Olin Mathieson) and 1-isopropenyl-o-carborane (Alfa Inorganics) were vacuum sublimed twice with an Ace Glass No. 8022-10 sublimator with the cold surface at 0° and the solid at about 50°. The pressure above the solid during sublimation was kept about 0.01 Torr. 1-Allyl-o-carborane (Olin Mathieson, 85% assay) was vacuum-distilled and the fraction distilling at 157° and 20 Torr was collected. 1-Ethyl-o-carborane and 1-n-propyl-o-carborane were obtained by catalytic hydrogenation of 1-vinyl and 1-allyl-o-carborane in hexane with 30 psi hydrogen at 23° over a palladium-on-carbon catalyst in a Parr hydrogenator. The catalyst was filtered from the 1-alkyl-o-carborane solution and the solvent was evaporated. The 1-ethyl-o-carborane was twice vacuum-sublimed with the solid at 30° and yielded a plastic crystalline[1] solid melting at 37°. The liquid 1-n-propyl-o-carborane was eluted from a 1/2-in. x 4-in. column of activated silica gel with purified cyclohexane and was recovered by vacuum evaporation of cyclohexane. All carboranes used were shown to be more than 99% pure by gas chromatography. For optical study, a trace of impurity absorbing near 270 nm was eliminated from 1-vinyl, 1-ethyl, and 1-allyl-o-carborane by eluting each carborane from

a 1/2-in. x 18-in. column of activated silica gel with purified cyclohexane followed by solvent evaporation and vacuum sublimation of the remaining solid.

The cyclohexane (Mallinckodt, Spectroquality) was passed through a 2.4-cm x 1.5-m column of freshly activated 20-200 mesh silica gel and fractions were rejected if the absorbance of deaerated eluent vs. distilled water exceeded 0.1 at 190 nm in a 1-cm cell. 2-Methyltetrahydrofuran and 3-methylpentane (both Matheson Coleman and Bell, Chromatoquality) were passed through a column of activated 20-200 mesh silica gel before use. Triethylamine (Eastman Kodak) was purified by distillation. All other chemicals were the best available commercial grades and were used as received.

Unless otherwise stated, all experiments were performed with deaerated solutions prepared by 5 or more freeze (77°K)-pump-thaw cycles or deaerated solids prepared by 3 or more vacuum sublimations. For EPR or low temperature optical studies, the final cycle of deaeration included transfer and sealing into a fused silica EPR tube or 1-cm x 1-cm curvette attached to the deaerating bulb.

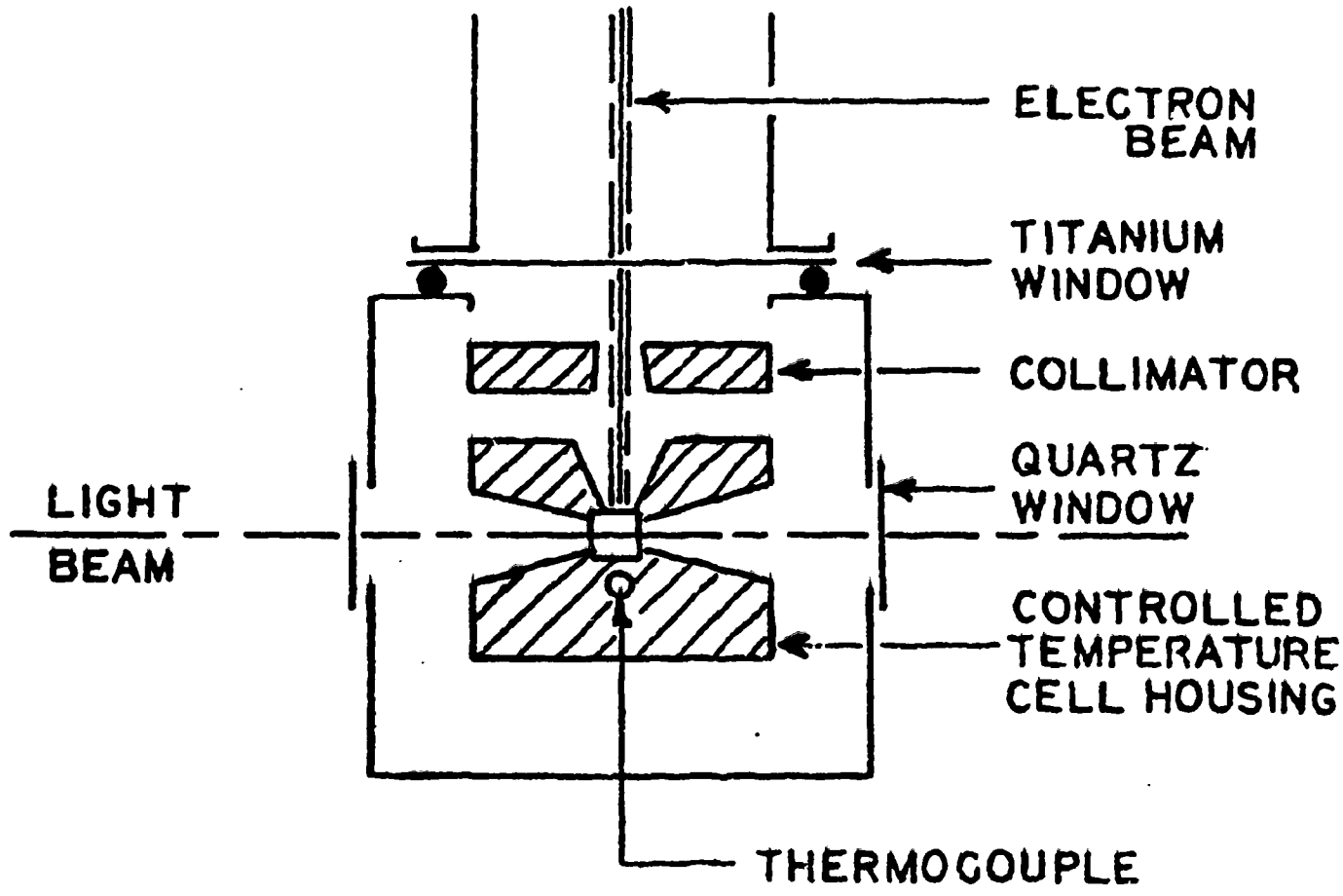
Gas Chromatography-- An Aerograph 202 gas chromatograph with thermal conductivity detector was used to measure the initial yields of volatile products (not condensed at 77°K) from radiolysis of 1-allyl-o-carborane and cyclohexane solutions of the carboranes. Total gas yields were calculated using the ideal gas law with measured pressure and temperature for the gas collected from an irradiated tube via a breakseal into a calibrated volume by means of a Toeplar pump and repetitive freeze (77°K)-pump-thaw cycles. Gases were separated with a 1/4-in. x 8-ft column packed with 80-100 mesh Poropak® Q and were identified by comparison of retention times

with those for reagent gases introduced to the column under identical conditions.

During this report period, a departmental Beckman GC-5 gas chromatograph with flame ionization detection became available and was used to measure initial yields of nonvolatile (at 77°K) products from radiolysis of cyclohexane solutions of carboranes. Cyclohexene was separated from cyclohexane with a 1/4-in. x 6-ft column packed with 60-80 mesh firebrick coated with 20 wt % of a solution of 33% $AgNO_3$ in glycerol. The carboranes, dicyclohexyl and cyclohexylhexene were resolved with a 1/4-in. x 1-m column packed with 60-80 mesh Gaschrom® Q coated with 20 wt % Carbowax 20M. Other high temperature separations were performed with a 1/4-in. x 1-m column of 60-80 mesh Chromosorb® P coated with 20 wt. % SE-30. Concentration of radiolysis product was measured from peak areas; detector response was calibrated with standard solutions before and after each series of measurements. The variance for such measurements is estimated to be near 15%.

Electron Accelerator-- The University's 3.0 MeV Dynamitron accelerator, as described in ORO-3781-9, is now available to this project. During the past project period, a full-time operator, retained by the University, has completed electrical overhaul of the machine and installation of a new target assembly including a water-cooled copper target, an optional 0.002-in. thick titanium window and a temperature-controlled cell holder shown in Figure 1. A typical dose rate to the oxygenated ferrous sulfate dosimeter for bremsstrahlung is $3.15 \times 10^{20}$ eV $g^{-1}hr^{-1}$ with 6 mA beam current at 2 MeV on the copper target. For electron radiation through the

Figure 1. Controlled temperature cell housing for Dynamitron accelerator



titanium window, a dose rate of $1.3 \times 10^{22}$ eV $g^{-1}$ $hr^{-1}$ for a beam current of 1.0 μA at 2.0 MeV has been measured with the cerric sulfate dosimeter. Dose rates at 2 MeV are proportional to beam current with a 10-mA maximum presently available.

Components and accessories for a single beam optical spectrometer (Figure 2) used with the temperature-controlled cell holder have been obtained. Light from an American Ultraviolet 450 watt xenon lamp in an Oriel universal lamp housing, Model C160-50, is focused with 2-in. fused silica lenses through the cell to the entrance slits of a Heath Schlumberger monochromator, Model No. EU-700, with photomultiplier detector module, Model No. EU-701-30. Photomultiplier output is observed with either a Techtronics dual channel oscilloscope, Model 7623, equipped with a synchronous camera, Model No. C51P, for fast (1 nsec resolution maximum) signals or a strip-chart recorder for slower signals. During the next project period, a pulsed electron gun[2] will be installed and provide electron pulses of duration 1 to 100 nsec. A pulsing circuit for the xenon lamp will be built to provide maximum light output for about 0.2 msec after triggering by the electron pulse. A mechanical beam chopper will become available to intersect the continuous beam and produce pulses of duration longer than about 1 msec.

Analytical Liquid Chromatography-- During this report period, a Waters Associates analytical liquid chromatograph, Model ALC-201, was used extensively for qualitative characterization of molecular weight distributions of polymers and separation of molecular weight fractions for analysis by other techniques. The versatility of

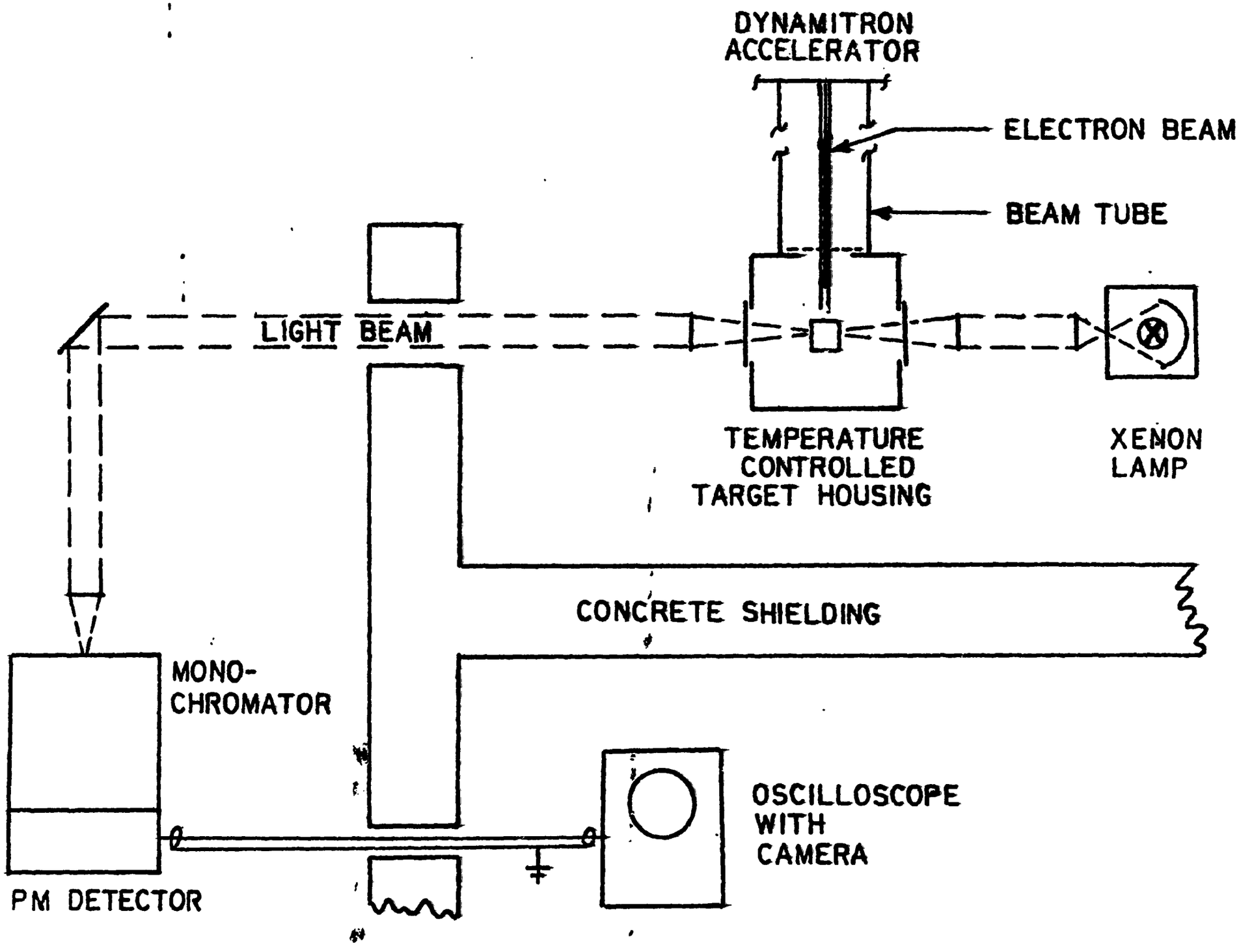



Figure 2. Single beam UV-Vis spectrometer for use with Dynamitron accelerator.

the instrument was greatly increased by recent acquisition of four additional 3/8-in. x 4-ft gel permeation columns of Poragel® 200 Å and Styragel® $10^3$ Å, $10^4$ Å and $10^5$ Å. This range of columns together with a similar Poragel® 100 Å column described in ORO-3781-9 will permit quantitative measurement of molecular weight distributions of polymers[3] with a molecular weight upper limit of about $2 \times 10^6$.

Optical Spectroscopy-- Absorption spectra of the carboranes in cyclohexane solution at 23° were recorded on a recently available Cary 17 spectrometer. A variable temperature accessory, Figure 3, was constructed for this instrument and the spectrum of the trapped electron in MTHF near 77°K was obtained as shown in Figure 8 . Other spectra near 77°K were obtained in this accessory. Deaerated solutions were sealed in 1-cm x 1-cm fused silica cuvettes and were exposed to Co-60 gamma radiation at 77°K for a dose of about $1.2 \times 10^{18}$ eV $g^{-1}$. A departmental Aminco-Bowman spectrofluorimeter also became available and was modified with an 1P28 phototube for use in the ultraviolet region and used to examine the carboranes for fluorescence.

Electron Paramagnetic Resonance-- The EPR experiments are described in ORO-3781-9 and are essentially unchanged. Dose rate for Co-60 irradiation was about $3.6 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$ and total dose was usually $1.2 \times 10^{18}$ eV $g^{-1}$.

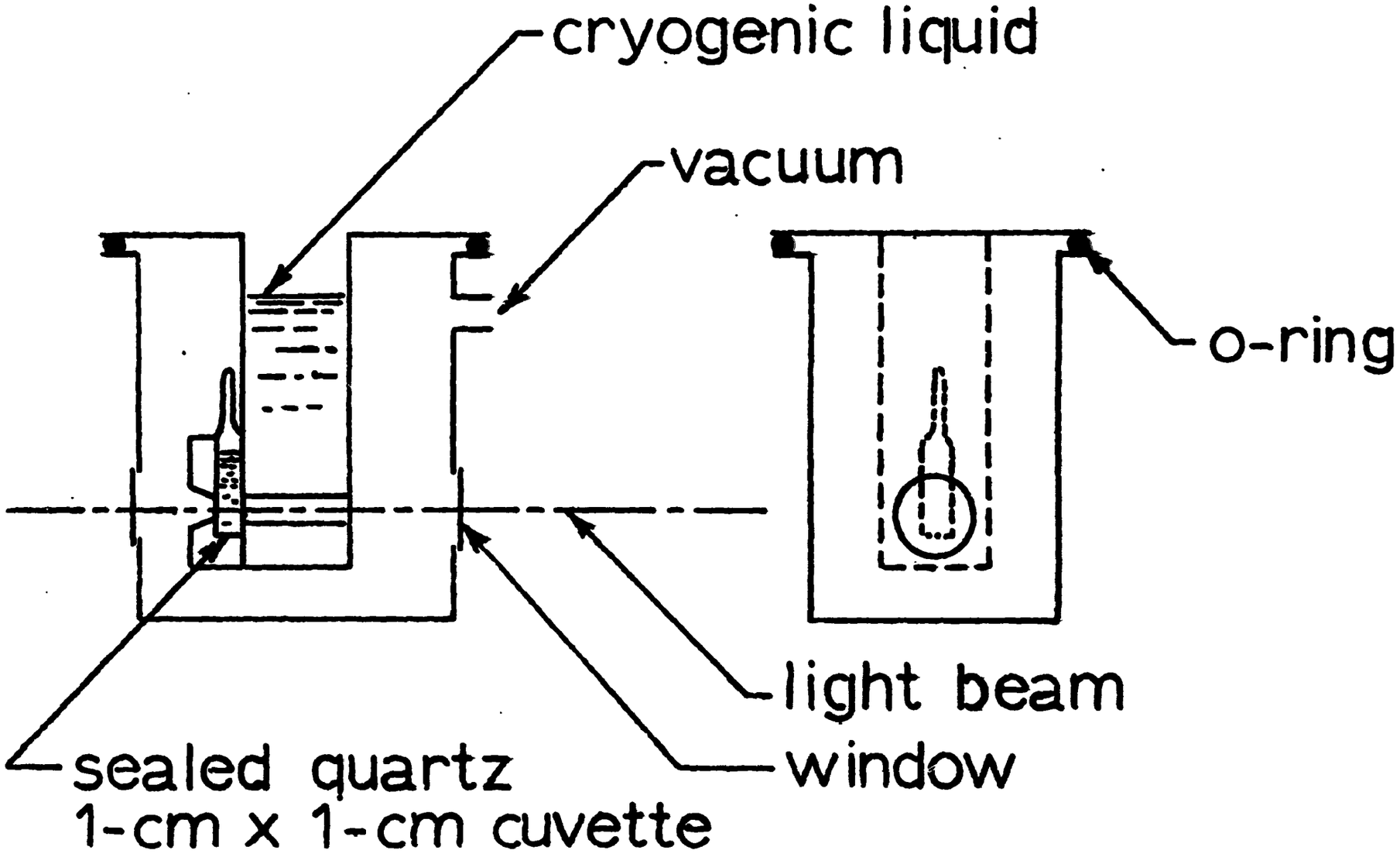



Figure 3. Low temperature accessory for Cary 17 spectrometer

## RESULTS AND DISCUSSION

### Electron Paramagnetic Resonance of Carborane Radicals

Study of EPR spectra of irradiated solid carboranes at 77°K, as reported in ORO-3781-9, suggested that at least two types of radicals are present; one producing a broad EPR singlet characteristic of a carborane cage radical which is the only radical seen for o-carborane (OC), Figure 4, and another producing a hyperfine pattern with hyperfine splitting constants characteristic of the most stable form of substituent alkyl radical. The spectrum for irradiated 1-ethyl-o-carborane (EOC), Figure 5A, identifies the substituent alkyl radical as the $\theta(CH_3)CH\cdot$ radical ($\theta$ denotes the o-carborane cage, $B_{10}C_2H_{11}$-). Warming followed by rapid cooling to 77°K leads to Figure 5B; the $\theta(CH_3)CH\cdot$ increases and the singlet of the cage radical is completely eliminated. The spectrum for irradiated 1-vinyl-o-carborane (VOC) at 77°K, Figure 6A, shows only a small amount of $\theta(CH_3)CH\cdot$ radical suggesting either a low yield of hydrogen atoms or inefficient hydrogen atom scavenging by the vinyl double bond. Warming followed by rapid cooling to 77°K causes a decrease in the singlet of the cage radical as shown in Figure 6B similar to the decrease observed for EOC, but no increase in the amount of $\theta(CH_3)CH\cdot$ is observed. The EPR spectra of irradiated EOC and VOC at 77°K are typical of those found for the other 1-alkyl and 1-alkenyl-o-carboranes, examples of which are shown in ORO-3781-9. Additional study of these solids by variation of method of preparation, purification and deaerating or of rate of cooling has not changed these observations. Additionally, photolysis with 313-nm

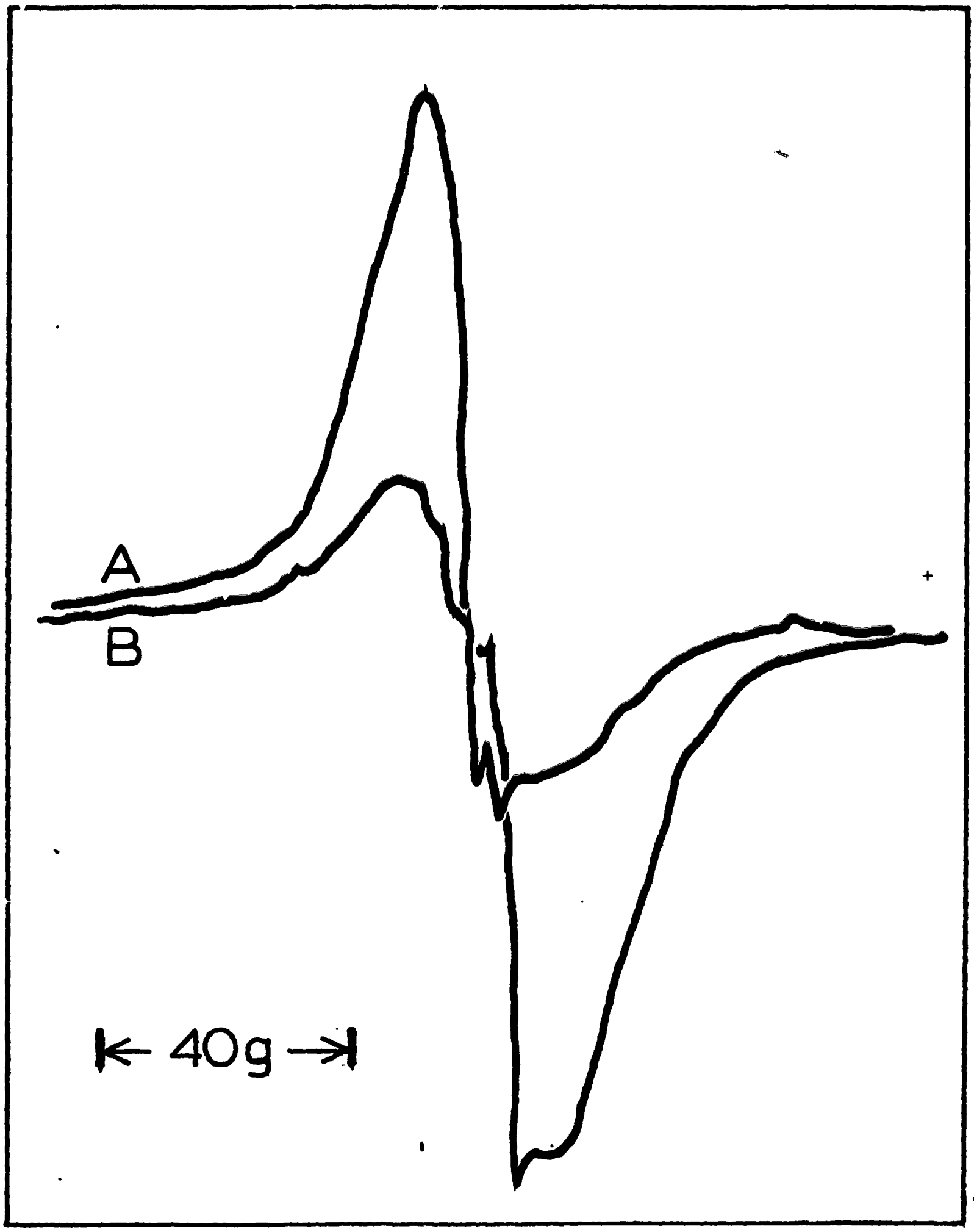



Figure 4. EPR spectrum of γ-irradiated pure o-carborane at at 77°K, immediately after radiolysis (A) and after warming and quick recolling to 77°K (B).

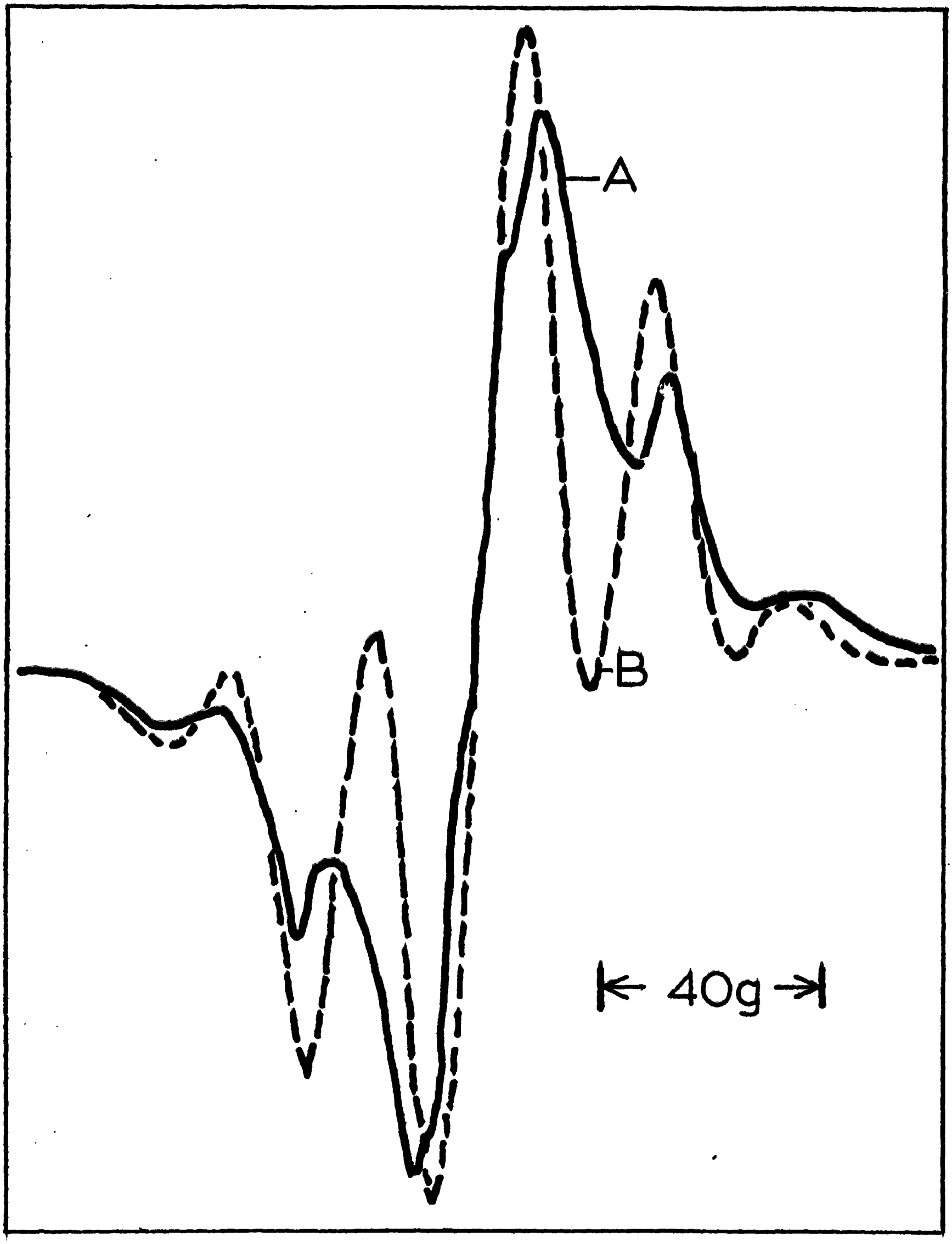



Figure 5. EPR spectrum of γ-irradiated pure 1-ethyl-o-carborane at 77°K, immediately after radiolysis (A) and after warming and quick recooling to 77°K (B).

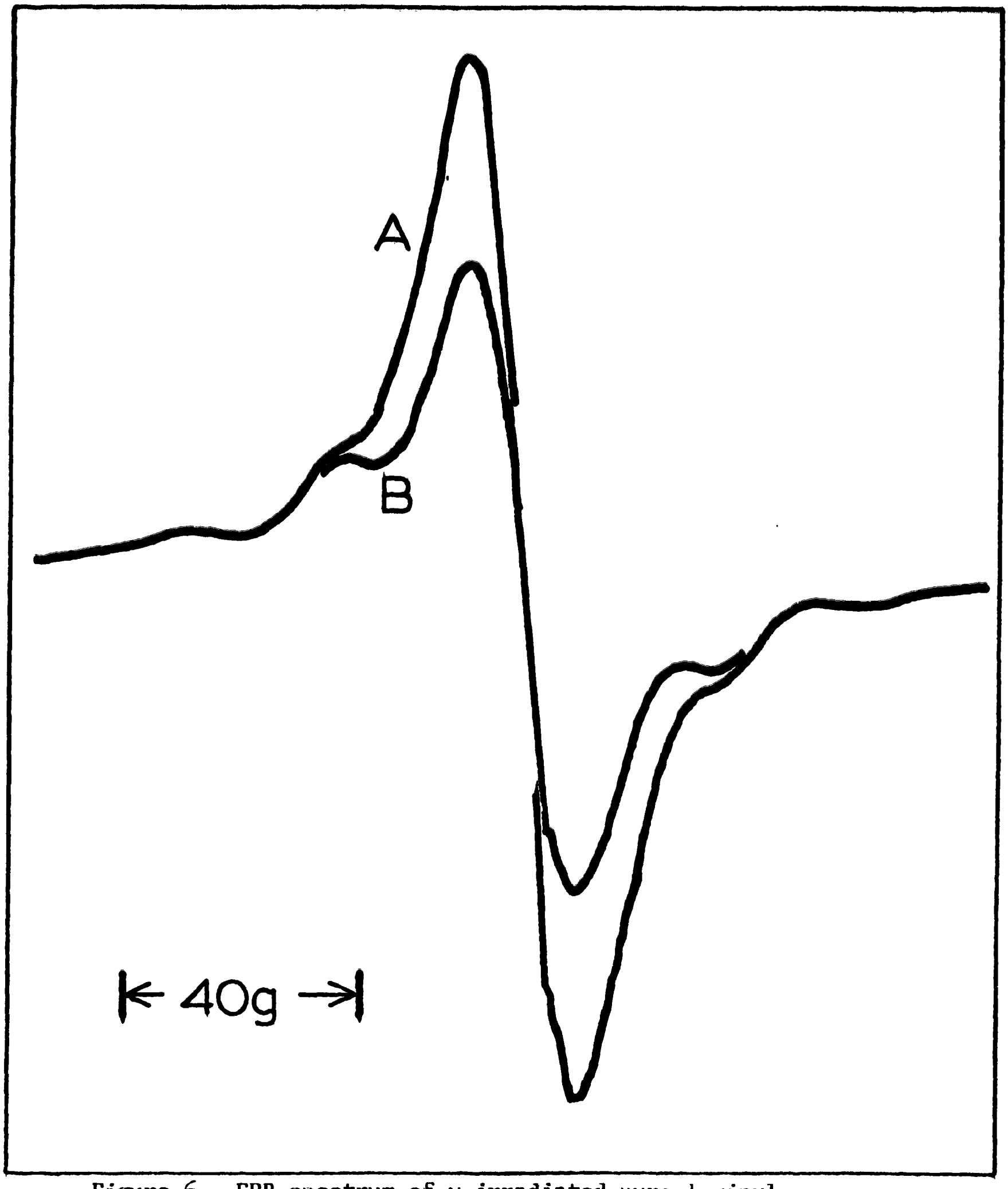



Figure 6. EPR spectrum of γ-irradiated pure 1-vinyl-o-carborane at 77°K, immediately after radiolysis (A) and after warming and quick recooling to 77°K (B).

light eliminates some of the cage radical causing the singlet; the apparent efficiency was different for each carborane. This latter observation, however, is complicated by obvious variation of the fraction of incident light scattered from the polycrystalline solids.

A study of gamma-irradiated solutions of carboranes at 77°K shows that the cage radical is quite stable with respect to hydrogen abstraction from the hydrocarbon solvent. EPR spectra typical of those obtained in such experiments at 77°K are shown in Figure 7 where spectrum A is the radical spectrum recorded for pure irradiated MTHF, spectrum B shows the EPR spectrum of the solvent radical of MTHF with an underlying singlet in MTHF containing 2 mole % OC and spectrum C is obtained for the same solution shown in spectrum B after warming the EPR tube until melting of the solution is obvious and quickly recooling to 77°K. Spectrum C, although shown here at slightly higher gain than B, is remarkably persistent, decaying slowly with a half life of about one minute only after complete melting of the solid solution.

The same behavior is observed for solutions of carboranes in 3-methylpentane (3MP), 3MP with 5 mole % triethylamine (TEA), 3MP with 5 mole % 2-methylpentene-1 (2MP), and MTHF. Furthermore, although solid solutions of o-carborane and 1-ethyl, 1-vinyl, 1-allyl, 1-phenyl, and 1-isopropenyl-o-carborane were examined, the spectra observed never differed from that shown in spectrum C and the solvent radical hyperfine structure always is identical for the solution and pure solvent spectra as in Figure 7. An important exception to the foregoing observations is the absence of spectrum C in irradiated solid solutions of carboranes in n-butyl chloride;

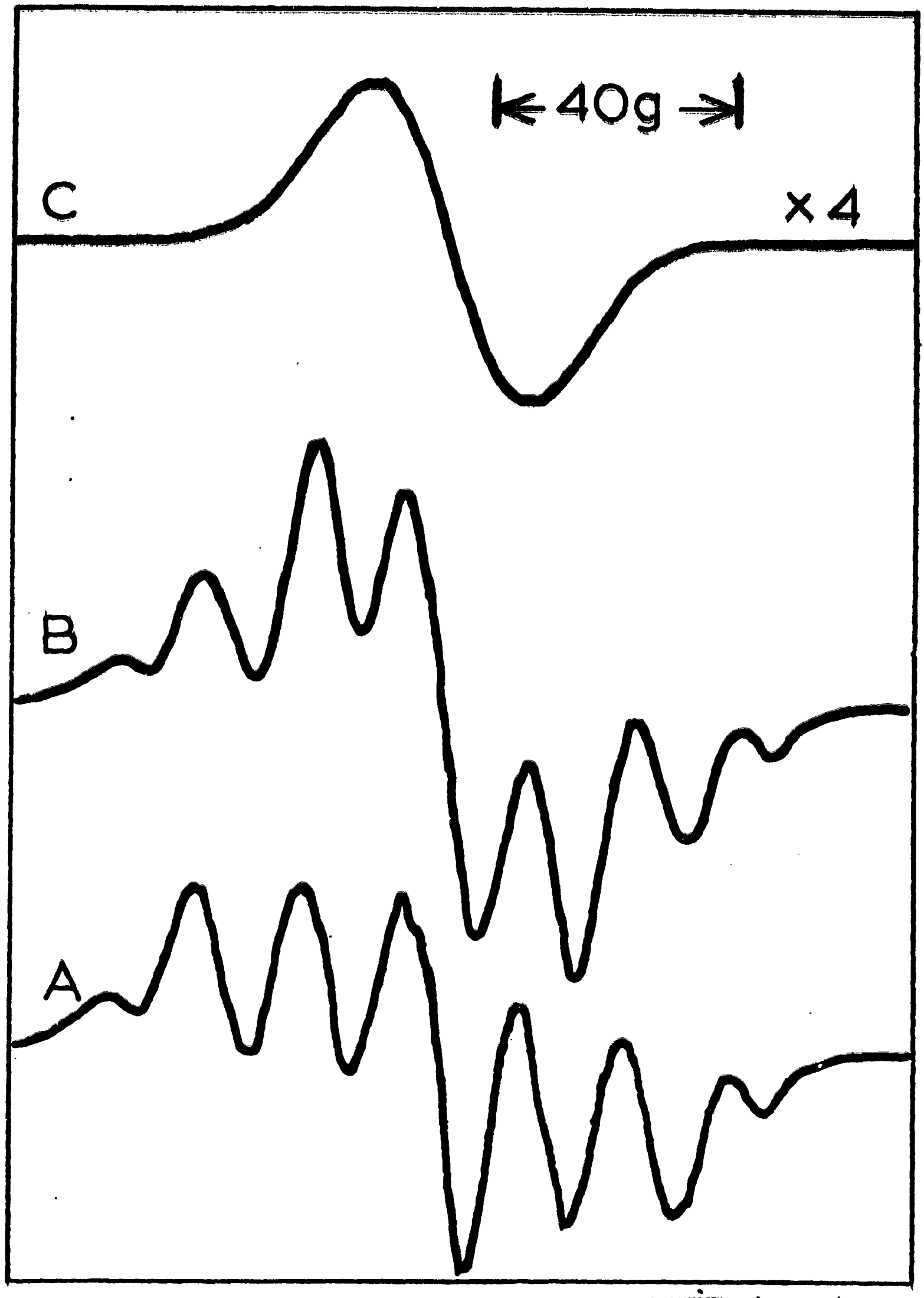



Figure 7. EPR spectra observed in γ-irradiated MTHF glass at 77°K. A--irradiated pure MTHF glass containing 2 mole % o-carborane. C--same glass as in B after warming until melting is observed and then quickly recooling to 77°K.

only the n-butyl radical is observed in both pure solvent and solution.

The EPR spectra of the irradiated solid solutions and the spectral changes caused by warming are consistent with the interpretation offered for the EPR spectra of the irradiated pure solids. From the absence of the cage radical in n-butyl chloride, which captures electrons by electron-dissociative attachment,[4] electron capture by the cage is inferred as the precursor of the cage radical. It is unlikely that the cage radical is the carborane anion, however, because cation scavengers such as TEA and 2MP and the cation-trapping solvent MTHF[4] did not increase the intensity of the singlet compared to that in 3MP as would be expected if the singlet were caused by an anion; also the singlet spectrum has a long half-life even after melting which would cause much more rapid ion recombination. A cage radical caused by loss of a boron-bonded hydrogen atom is an alternative assignment which is consistent with the results. Several important characteristics of the cage radical are suggested by this interpretation.

The bond dissociation of the boron-hydrogen bond must be less than that of any molecular hydrogen of the hydrocarbon solvents or solutes as shown by the persistence of the cage radical after disappearance of all solvent radicals. Hydrogen abstraction from the solvent might have been expected if this were not the case. Indeed, the opposite may be occurring with solvent radicals abstracting hydrogen from the cage. Such abstraction by solvent radicals and perhaps slow coupling of cage radical owing to steric hinderance of boron-boron bond formation may explain the rather

slow disappearance of the cage radical after melting. At low temperatures, the diffusion rate of the carborane cage may also be much slower than that of solvent radicals.

For pure solids, the cage radical disappears after warming by coupling to form dimers, by addition to the double bonds of 1-alkenyl-o-carboranes, and by abstraction of active hydrogen from the alkyl group of a neighboring 1-alkyl-o-carborane. The first mode of disappearance is responsible for the presence of the vinyl group in the NMR spectrum of the oligomeric radiolysis product from irradiated VOC after it has been repeatedly washed free of monomer.[5] The second mode is consistent with the proposed through-the-cage-bonded structure for one of the two oligomeric radiolysis products; this structure was suggested by NMR and infrared spectra of the oligomers.[5,6] Addition, however, must be a slow process compared to coupling when diffusion is allowed because no EPR evidence for addition was seen during melting of solid solutions and disappearance of the cage radical, even in solutions containing 5 mole % 2MP. Addition of the cage radical to a double bond in the solid must occur slowly with a nearest neighbor.

Abstraction of active hydrogen by the cage radical, the third reaction, is suggested by warming of irradiated pure 1-alkyl-o-carboranes; the cage radical spectrum disappears and the substituent alkyl radical spectrum increases, e.g, EOC in Figure 5. (Some substituent alkyl radical obviously arises initially via hydrogen abstraction by atomic hydrogen or, in the case of alkenyl

substituents, by addition to the double bond. This however occurs only in pure carboranes; in solid solutions reaction of atomic hydrogen with solvent apparently predominates.) Each cage radical in the pure solid may abstract an active alkyl hydrogen from one of its nearest neighbors. Warming supplies the necessary activation energy. Coupling is not important because diffusion is slow relative to abstraction. Similar behavior is expected and observed for 1-allyl-o-carborane because the β hydrogen is active and abstraction forms a stable allylic radical. The abstraction reaction apparently is not intramolecular because the cage radical only is observed in irradiated solid solutions. Intermolecular abstraction from solute in such solutions does not occur as shown by the absence of the substituent alkyl radical spectrum during or followed loss of the cage radical spectrum; presumably the coupling reaction is kinetically competitive with abstraction. If these arguments are sound, an interesting result is the establishment of an order of bond dissociation energies. The bond between carbon and active-hydrogen in carborane alkyl substituents must be of lower energy than the boron-hydrogen bond because of the abstraction reaction in irradiated pure solid. The boron-hydrogen bond must be of lower energy than any carbon-hydrogen bond energies of the various solvents or solutes used, owing to absence of hydrogen abstraction from solvent. Furthermore, in view of the preferential halegonation of B(9) and B(12) boron atoms in halegon displacement reactions,[7] it now becomes of interest to isolate and characterize the cage radical, perhaps by using $I_2$ as a radical scavenger or by isolating the dimer coupling product.[9] Also, the possibility of assigning the cage radical to

the unsubstituted cage carbon, C(2), has not been mentioned thus far. There is no reason for eliminating this possibility, and this will be checked by studying the 1,2-disubstituted o-carboranes. Such irradiated carboranes would show an unchanged EPR spectrum if the radical is on a cage boron. If the cage radical is on C(2), the EPR spectrum of 1,2-disubstituted carboranes will either not show the singlet or will show the singlet and the radical eliminated from the C(2) carbon.

Earlier in this discussion the efficiency of photolysis of the irradiated solid carboranes with 313-nm light was reported to vary for each carborane owing to variation of the fraction of incident light scattered from the polycrystalline solids. Scattering is not a problem for the glassy solid solutions. The cage radical is photolyzed with about equal apparent efficiency for all carboranes with 313-nm light, but ordinary room lights are not effective. A small rapid decrease in the cage EPR singlet may indicate an initial amount of trapped anion, but the main fraction of the EPR spectrum must be assigned to the hydrogen-deficient cage radical. The 313-nm wavelength of the photolysis light almost coincides with the cage radical absorption maximum at about 320-nm (vide infra, UV Absroption of γ-Irradiated Glasses). The decrease in the EPR singlet accompanying photolysis may be caused by hydrogen atom elimination from the photo-excited radical, perhaps with decomposition of the cage. No evidence has been sought yet to substantiate these speculations, however.

Summary-- The EPR study indicates that electron capture is the precursor of the hydrogen-deficient cage radical which is the

most abundant radical in irradiated solid solutions. The bond dissociation energy for the boron-hydrogen bond is intermediate between the carbon-hydrogen bond energy of the hydrocarbon solvents and the bond energy of the bond between carbon and active hydrogen in the alkyl substituents of the carboranes. Formation of the chain-carrying alkyl radical for 1-alkenyl-o-carborane polymerization appears to be an inefficient process, owing perhaps to ease of displacement on B(9) hydrogen by hydrogen and alkyl radical initiators. (This topic is discussed more fully in the section, Radiolysis of Cyclohexane Solutions ...) Abstraction of substituent-alkyl active hydrogen by the carborane cage radical is efficient in the pure solid. This result suggests that perhaps a mixture of 1-alkyl and 1-alkenyl-o-carboranes would be more efficiently polymerized than 1-alkenyl-o-carboranes alone because cage radicals would be converted to substituent alkyl radicals capable of polymer initiation.

## Optical Spectroscopy of Irradiated Alkane Glasses at 77°K

Irradiation of the pure polycrystalline solid carboranes at 77°K causes the solids to become colored.[9] Although absorption spectra of such solids cannot be recorded owing to light scattering, characteristic spectra were expected from irradiated alkane glasses containing about 2 mole % of the carboranes. A device, shown in Figure 3, was built and maintained the glasses near 77°K while spectra were recorded on the Cary 17. Figure 8 and 9 show results for VOC and 1-isopropenyl-o-carborane (IPOC) in MTHF at 77°K. Also shown is the solvent-trapped electron spectrum in MTHF at 77°K

Figure 8. UV absorption spectra of γ-irradiated glasses at 77°K.

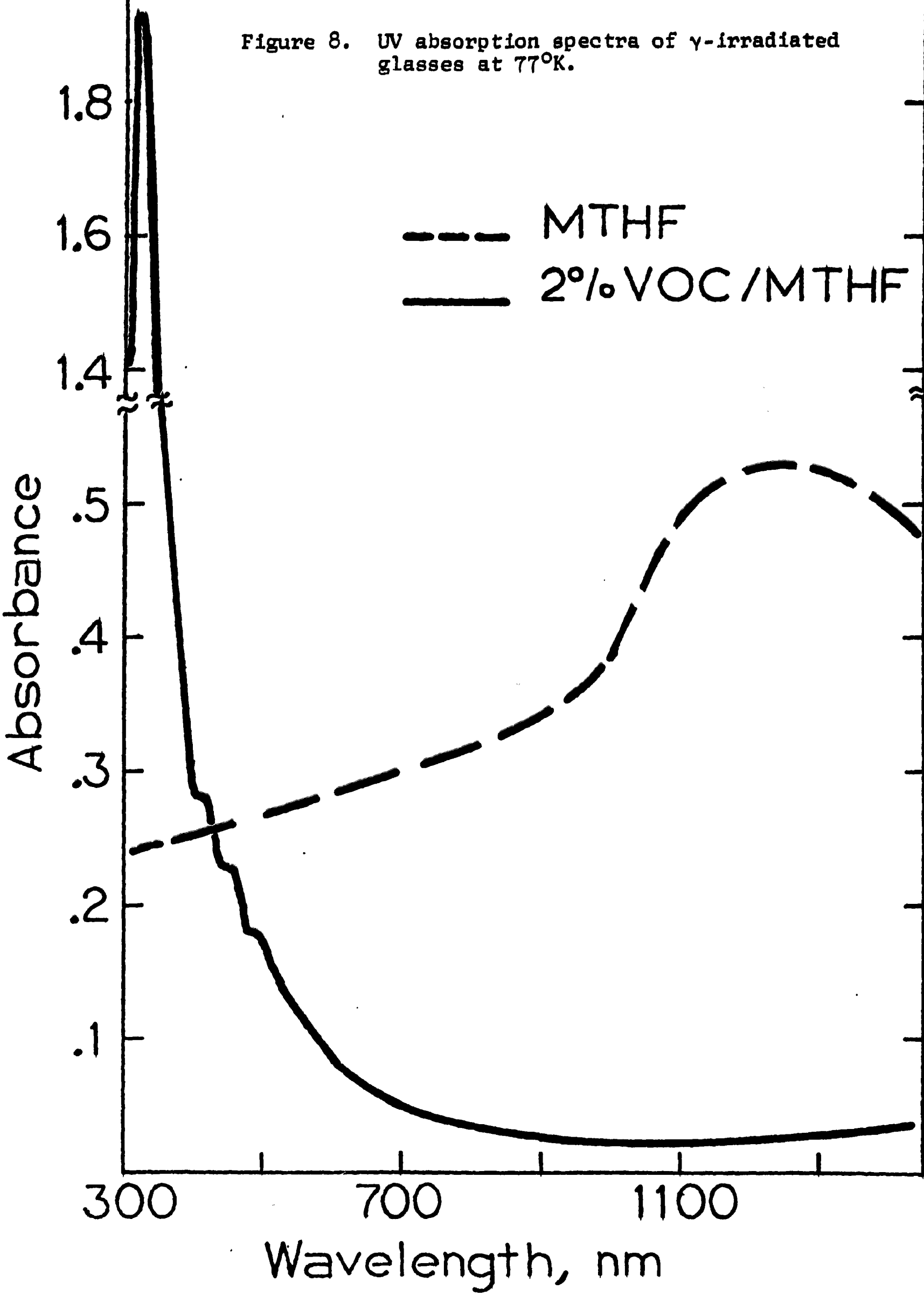
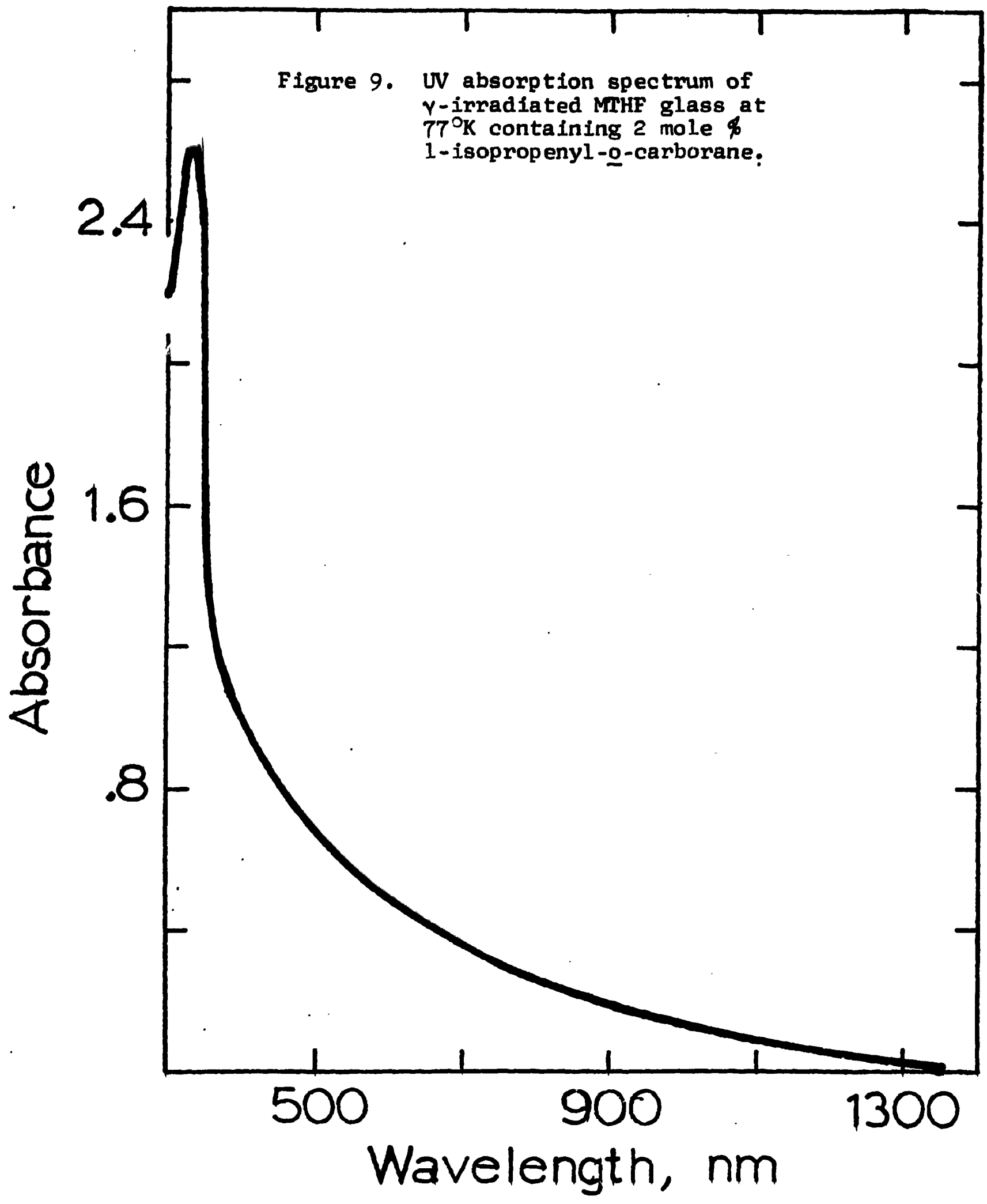


Figure 9. UV absorption spectrum of γ-irradiated MTHF glass at 77°K containing 2 mole % 1-isopropenyl-o-carborane.



obtained in these experiments. This spectrum with $\lambda_{max} \simeq 1300$ nm is in good agreement with that obtained by Hamill.[4] The electron spectrum is replaced by absorption in the ultraviolet with $\lambda_{max} \simeq$ 320 nm for the carborane solutions. The visible edge of this absorption imparts a yellow color to the glass in contrast to the green color observed previously[9] for the pure solid. Exposure to room light does not affect this spectrum; complete elimination of the absorption requires melting of the MTHF glass. This behavior is similar to that observed for the singlet radical spectrum observed by EPR in the previous section. The absorption might therefore be assigned to the cage radical seen by EPR. Absorption by hydrocarbon radicals occurs in this wavelength region. There is no reason for expecting carborane radicals to absorb at similar wavelengths, however. If further study shows this preliminary assignment incorrect and the absorbing molecule is a radical anion, it would be an unusually stable ion, indeed. For such to be true, the cation would also have to be stabilized by the carborane. Further work should elucidate these points.

Although several other glasses such as 3MP and TEA were tried, most gave badly cracked or opaque solutions with carboranes. Clear glasses were obtained with MTHF only with the two carboranes shown here. The cause of these diffuculties is at least partially owing to the high carborane content used.

## Copolymerization of 1-Vinyl-o-Carborane and Styrene

The well-studied radiation chemistry of styrene polymerization[3,10] suggested that styrene would be a good system to begin study of

radiation-initiated copolymerization of olefin monomers with 1-alkenyl-o-carboranes. Deaerated solutions of 6.8 mole % VOC in fractionally vacuum-distilled styrene were prepared with a technique similar to that of Potter, et al.,[10] using lithium aluminum hydride as the drying agent in place of BaO. The solutions and controls of pure styrene were irradiated from 2 to 60 hr at a dose rate of $4.5 \times 10^{19}$ eV $g^{-1}hr^{-1}$. The polystyrene obtained from controls was of low molecular weight compared to that obtained by other workers.[10] The polymer from irradiated solutions was of even lower molecular weight, e.g., the 20-hr exposure produced polystyrene with $\bar{M}_n$ = 4,700 and copolymer with $\bar{M}_n$ = 2,700. The use of lithium aluminum hydride as drying agent may be responsible for low molecular weights because the fine powder was observed in some cases to have blown over during transfer of styrene on the vacuum line into reaction tubes. This situation has been remedied by use of an in-line sintered glass filter. The decrease in $\bar{M}_n$ observed for copolymer relative to polystyrene may be caused by a slow addition step for the $\sim CH\theta CH_2\cdot$ radical which causes an increase in the steady-state concentration of such radicals with a consequent increase in termination rate.

After repeated washing of such polymers with chloroform, chloroform solutions of "copolymer" showed an infrared absorption at 3.85μ which is characteristic of carborane cage boron-hydrogen stretching frequency.[5] Although a quantitative study of the monomer ratio in the copolymer has not been completed, preliminary infrared comparison of the 3.85μ band with characteristic polystyrene bands suggest the carborane/styrene ratio is low. Such a

result might be expected if the probability of termination of polymer end radical, $\sim CH\theta CH_2\cdot$, is higher than that of the end radical, $\sim CH(C_6H_5)CH_2\cdot$, as has been suggested above. During the forthcoming report period, these speculations will be investigated using recently acquired equipment.[11]

## Radiolysis of 1-Vinyl-o-Carborane in Various Solvents

Wright and Klingen[5,12,13] have studied extensively the radiolysis of solid VOC and have found the main product to be low molecular weight oligomers. The low molecular weight of products from irradiated solutions of VOC in cyclohexane were attributed to a mixture of dimeric and trimeric carboranes by mass spectroscopy.[13] To ensure that this behavior is not unique to cyclohexane, deaerated solutions of VOC in each of five solvents were γ-irradiated for 24 hr at 31° with a dose rate of $3.6 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$ and compared with a cyclohexane solution of VOC treated identically by the methods of gas chromatography and analytical liquid chromatography (ALC). The solvents and mole fraction of VOC in the solutions were cyclohexane 0.14; benzene, 0.11; methanol, 0.06; acetone, 0.10; acetonitrile, 0.07; and carbon tetrachloride, 0.13.

The ALC chromatographs using a 100Å Poragel gel permeation column showed that no products of high molecular weight were formed in any solvent; all chromatographs were very similar to that of the cyclohexane solution. Gas chromatography on the SE-30 and Carbowax columns (see Experimental Section) showed no major peaks other than solvent and solute except for cyclohexane which is

discussed in a later section and for carbon tetrachloride. A series of six peaks are observed with retention times near that for the solute in carbon tetrachloride. The compounds corresponding to these peaks were not further analyzed, but probably result from a radiation-initiated free-radical chlorination of the carborane cage similar to that observed photochemically.[7] The results therefore suggest that solution polymerization of VOC does not occur for these six solvents and probably does not occur at all. Approximate G values calculated for products usually observed in cyclohexane[14] were found to be very low, particularly $G(H_2)$, and this led to a thorough study of irradiated cyclohexane containing carboranes, which is discussed in the next section.

## Radiolysis of Cyclohexane Solutions of the Carboranes[15]

A study of the high molecular-weight products from γ-radiolysis of cyclohexane solutions of 0.8 to 3.4 M VOC showed a G(-m) increasing from 7 to 12 in this range, which was attributed to carborane-dimer formation.[13] $G(EOC) \approx 1$ was also observed. From these results hydrogen-atom addition to vinyl can be inferred. The ethyl radical, $\theta(CH_3)CH\cdot$, must then couple to form dimer, disproportionate to form EOC and VOC, or perhaps abstract hydrogen from cyclohexane to form EOC, although the last reaction would not be consistent with the results of the EPR study discussed previously. The failure to find cyclohexyl adducts to VOC among the dimeric products[13] is surprising unless hydrogen abstraction of cage hydrogen from VOC is very rapid, indeed. Additionally, an estimate of $G(H_2)$ obtained in the work reported in the previous section was quite low and suggested a

strong "protecting" effect may exist in cyclohexane solutions of VOC. The following study was initiated to elucidate the mechanism of the radiolysis of cyclohexane solutions of VOC, to search for a "protecting" effect, to understand the reactivity of the $\theta(CH_3)CH\cdot$ radical, and, therefore, to explain the reason for the failure of VOC polymerization in solution. In order to establish the generality of conclusions drawn from the VOC study, irradiated cyclohexane solutions of OC, EOC, and AOC were studied and the results are compared with those from study of VOC radiolysis in cyclohexane.

Values of $\underline{G}(H_2)$, $\underline{G}$(cyclohexene) and $\underline{G}$(dicyclohexyl) from $\gamma$-radiolysis of deaerated cyclohexane solutions of OC, EOC, VOC, and AOC are shown in Figures 10 to 13, respectively, as plots of $\underline{G}$(product) $\underline{vs}$. solute concentration. For OC solutions, values of $\underline{G}$(cyclohexylhexene) also were measured and are shown in Figure 10. In VOC and AOC solutions, values of $\underline{G}$(cyclohexylhexene) were too low for accurate measurement and were not measured in EOC solutions. The solid lines are theoretical and are explained later.

Two high boiling products were found by gas chromatography in solutions of VOC and AOC and were assigned by mass spectrometry to products of the cyclohexyl radical coupling reaction with radicals of VOC and AOC. Approximate $\underline{G}$ values are shown in Table I. At the low conversions of these experiments, the amount of oligomeric products was insufficient for measurement and no loss of solute above 5%, the cumulative measuring error, was detected.

Values of $\underline{G}$(product) at the highest and lowest solute concentration for each solute were obtained from plots of yield $\underline{vs}$. dose; such plots were always linear through the origin. Doses were in the range $(3.6\text{-}18) \times 10^{18}$ eV $g^{-1}$ for measurement of $\underline{G}(H_2)$ and (5.4-22)

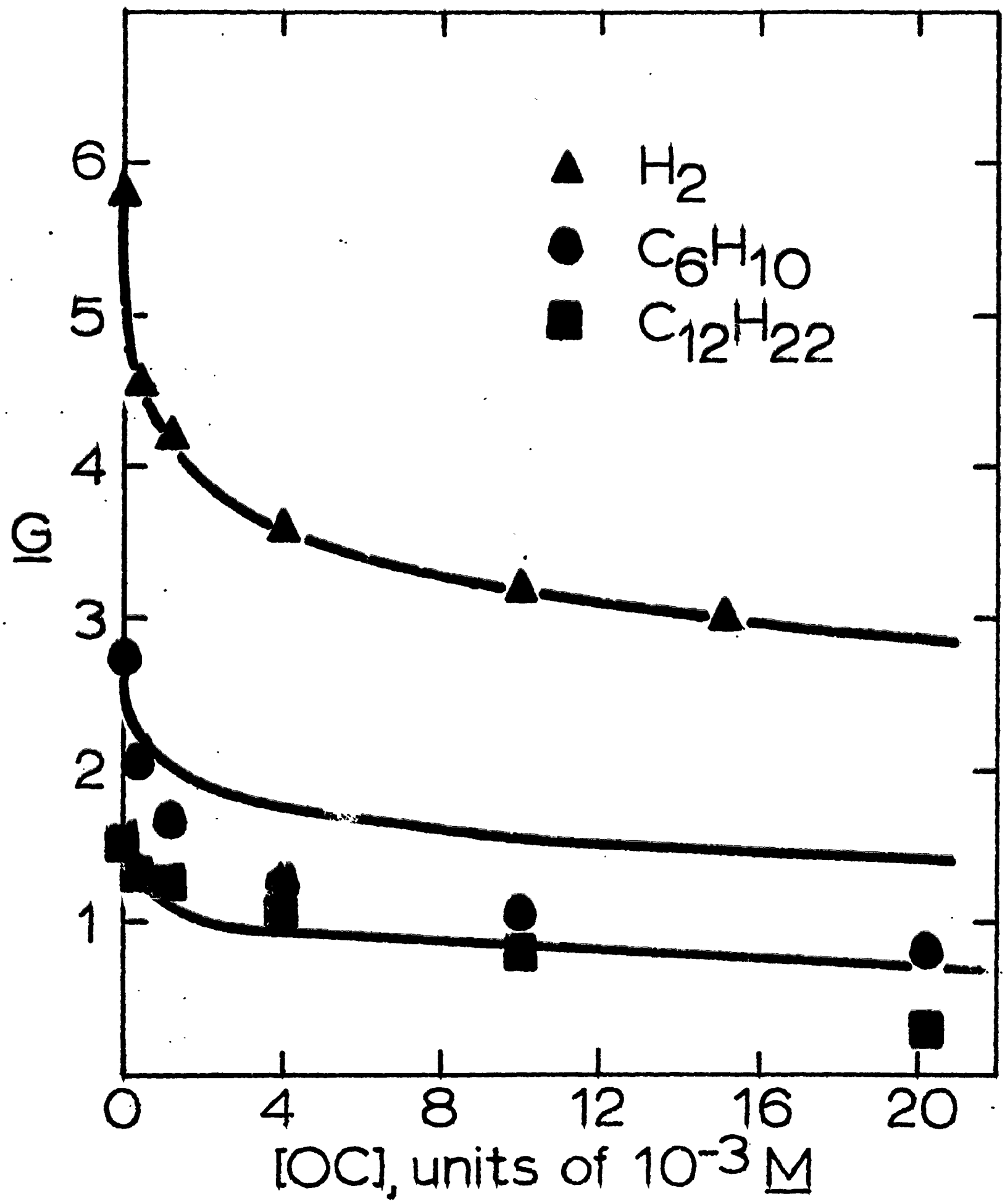



Figure 10. G-values for products from γ-irradiated cyclohexane solutions of o-carborane.

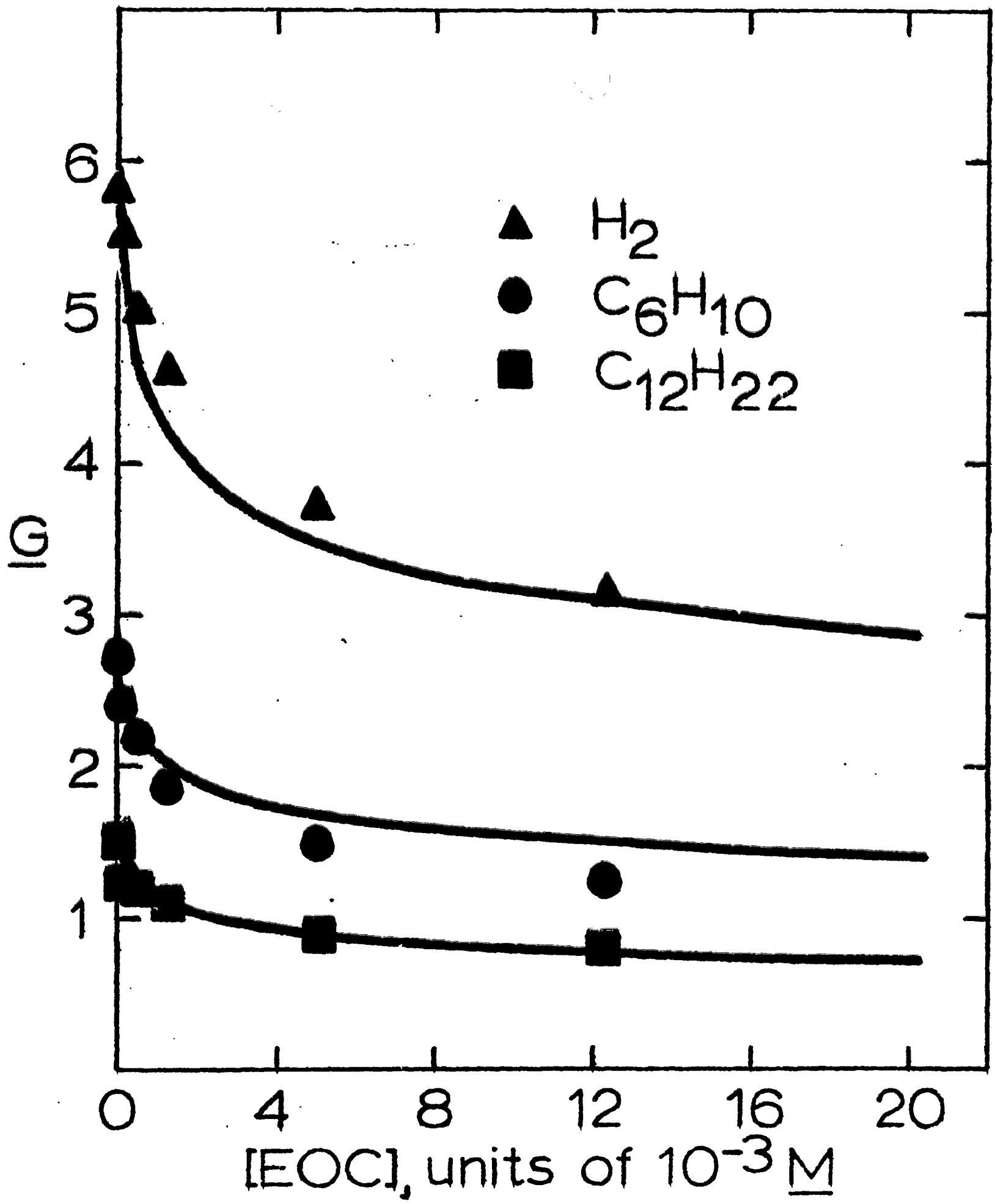



Figure 11. G-values fo. products from γ-irradiated cyclohexane solutions of 1-ethyl-o-carborane.

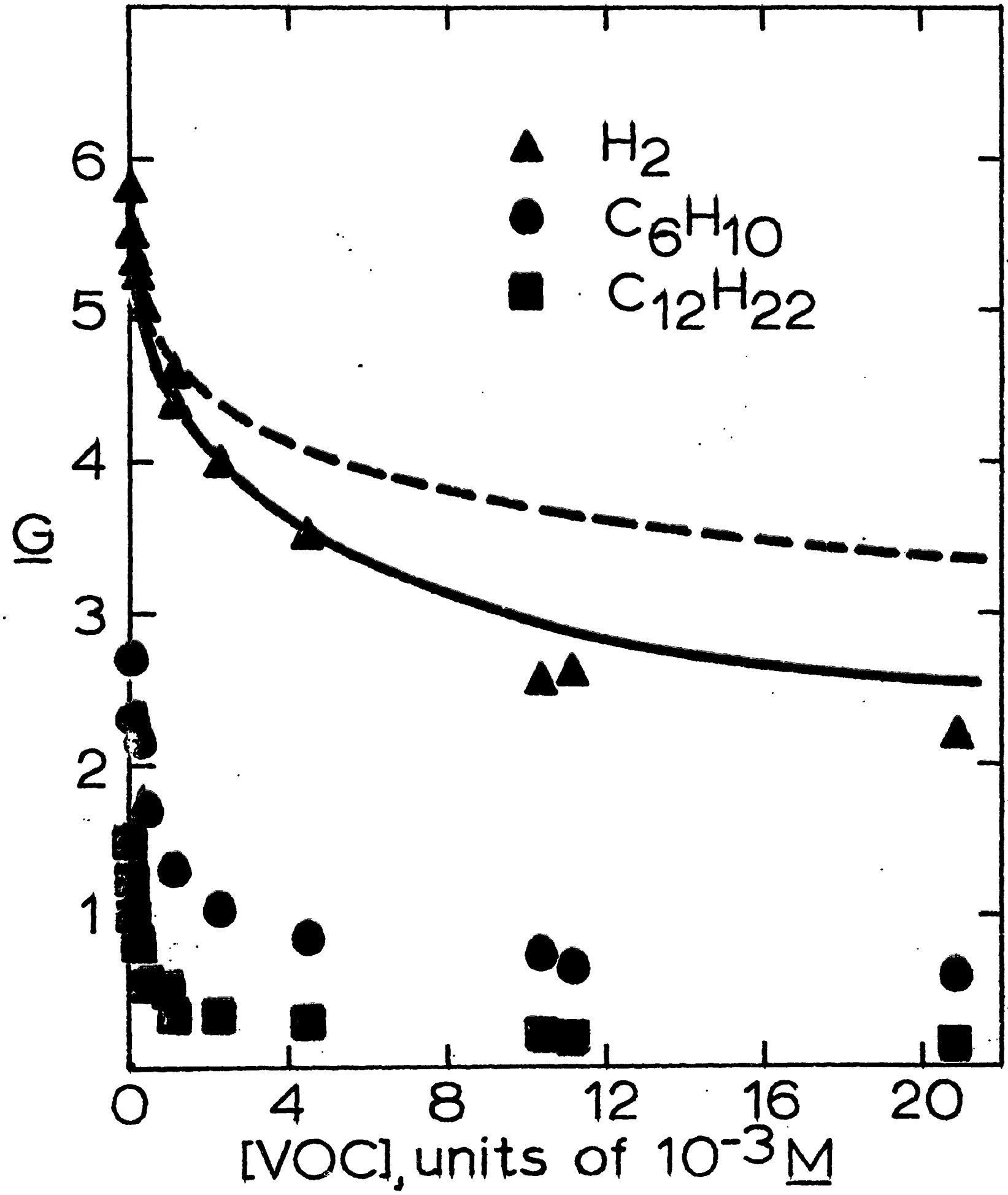



Figure 12. G-value for products from γ-irradiated cyclohexane solutions of 1-vinyl-o-carborane.

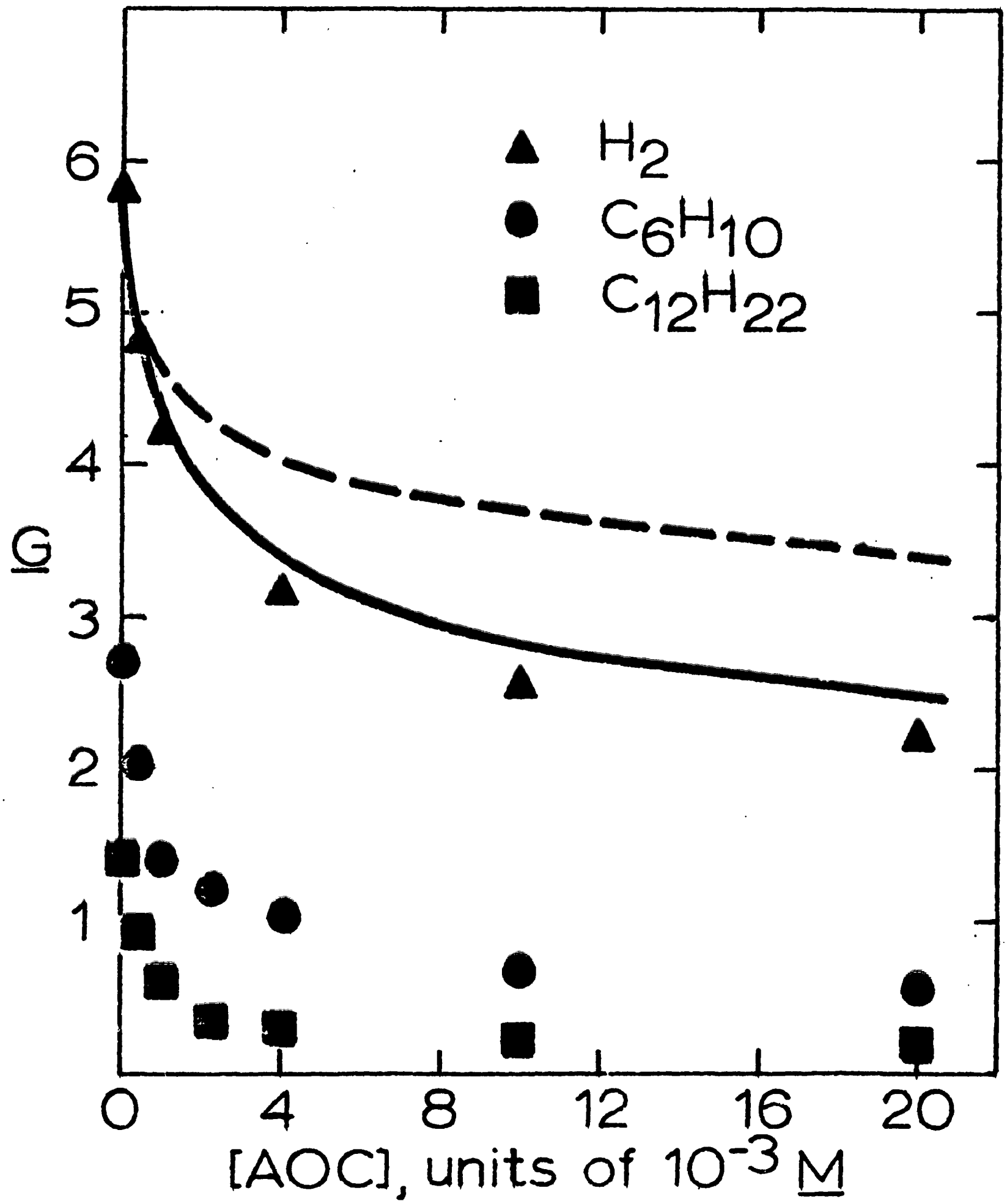



Figure 13. G-value for products from γ-irradiated cyclohexane solutions of 1-allyl-o-carborane.

TABLE I

G-Values for Cyclohexyl Adducts to
1-Alkenyl-o-Carboranes in Cyclohexane

| Solutes* | $G_1$† | $G_2$‡ | $G_{total}$ |
|---|---|---|---|
| VOC | 0.9 ± 0.2 | 1.5 ± 0.2 | 2.4 ± 0.4 |
| AOC | 1.2 ± 0.1 | 2.0 ± 0.3 | 3.2 ± 0.4 |

* Concentration range is 10-200 mM.

† Tentatively assigned to 1-(2-cyclohexylethyl)-o-carborane for VOC and to 1-(3-cyclohexylpropyl)-o-carborane for AOC.

‡ Tentatively assigned to 1-(2-cyclohexenylethyl)-o-carborane for VOC and to 1-(3-cyclohexenylpropyl)-o-carborane for AOC.

x $10^{19}$ eV $g^{-1}$ for measurement of other products.

Hydrogen Yields-- The value of $\underline{G}(H_2)$ = 5.8 found for pure cyclohexane is in fair agreement with the values of other workers,[14,16,17] but the values of $\underline{G}(C_6H_{10})$ = 2.7 and $\underline{G}(C_{12}H_{22})$ = 1.4 are both about 0.5 of a $\underline{G}$-unit lower than values given by most other workers.[14] No reason for this discrepancy was obvious because an adventious impurity capable of reacting with the cyclohexyl precursors of $C_6H_{10}$ and $C_{12}H_{22}$ would be expected to depress the $\underline{G}(H_2)$ also. The possibility of a systematic error in response calibration of the gas chromatographic detector or dosimetry was checked and does not seem likely. Although the absolute values may be somewhat in error, the effect of added carborane solute is not in doubt. Figures 10 to 13 show that yields of all measured products of cyclohexane radiolysis are decreased. Closer inspection shows that VOC and AOC are more efficient in this regard than are OC and EOC at any given concentration.

The dependence of $\underline{G}(H_2)$ on carborane concentration is quite similar to that observed for good electron scavengers.[17] If the carborane cage is assumed to react with the free and geminate electrons prior to recombination with solvent cations, the inhomogeneous scavenging equation I, introduced by Schuler and co-workers,[16,17,18] may be applied.

$$\underline{G}(H_2) = 1.8 + 3.9\left[1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right] \qquad (I)$$

The value of $\underline{G}(H_2)$ = 1.8 represents the estimated yield of hydrogen which is formed without a free or geminate electron-cation pair

precursor while $\underline{G}(H_2) = 3.9$ is the yield of hydrogen with an electron-cation precursor, i.e., it is the G-value of scavengeable electrons. The term $\alpha$, analogous to a specific rate constant ratio, is an empirical parameter which describes the inhomogeneous competition of electron capture by a solute of concentration, S, and electron-cation recombination. The quantity in parentheses is the probability that the electron will not be captured by solute, i.e., one minus the fraction which are captured. High values of $\alpha$ for a solute are identified with a large electron-capture cross-section, e.g., $N_2O$ with $\alpha = 16\ \underline{M}^{-1}$, $SF_6$ with $\alpha = 18\ \underline{M}^{-1}$, $CH_3Br$ with $\alpha = 16.2\ \underline{M}^{-1}$ and $\underline{c}\text{-}C_6F_{12}$ with $\alpha = 25\ \underline{M}^{-1}$.[17,18]

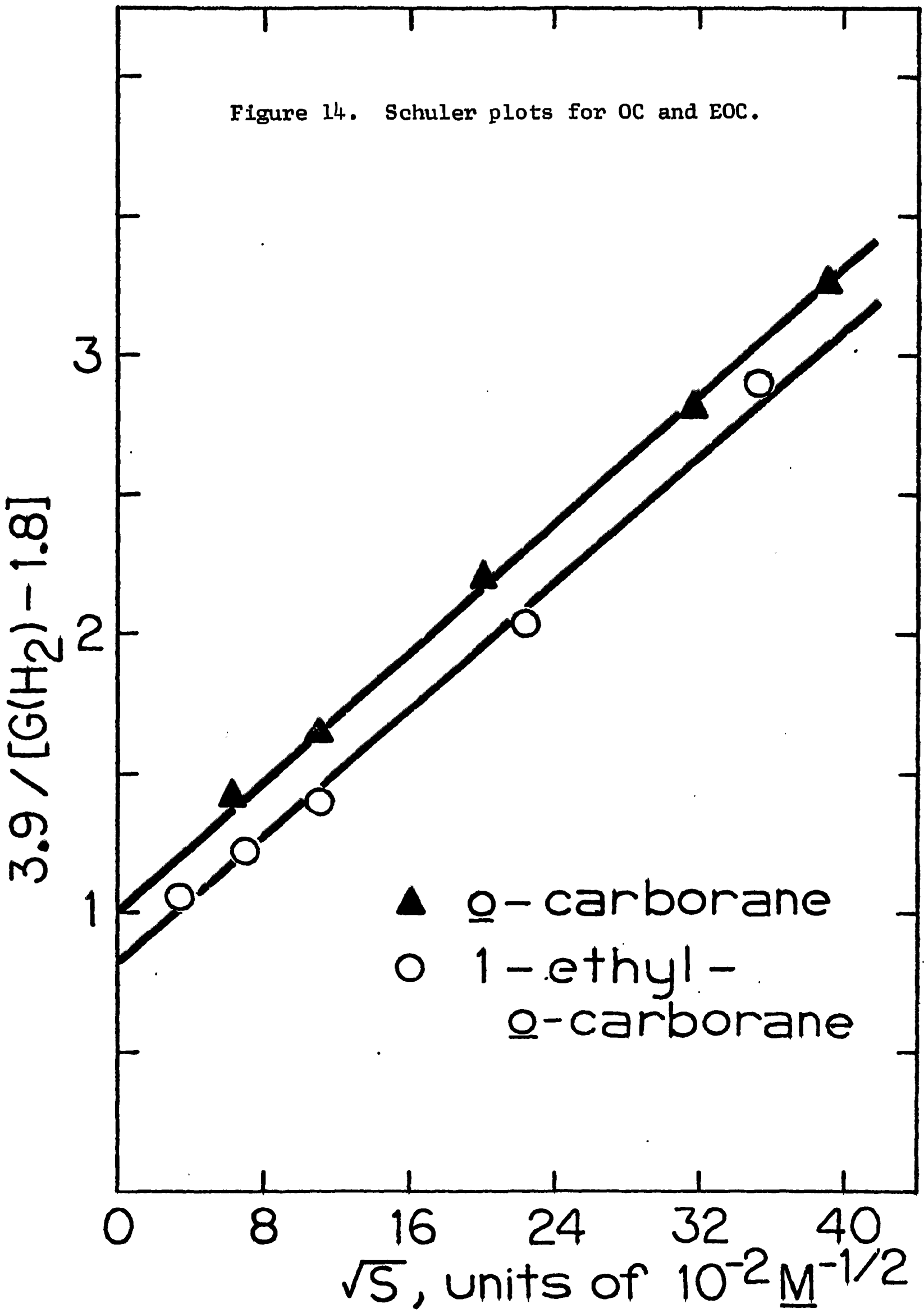
Rearrangement of equation I leads to equation II

$$\frac{3.9}{\underline{G}(H_2)-1.8} = 1 + (\alpha S)^{\frac{1}{2}} \qquad \text{(II)}$$

which is of linear form if the left hand side, calculated from measured values of $\underline{G}(H_2)$, is plotted vs. $S^{\frac{1}{2}}$. Application of equation II to the hydrogen yields from cyclohexane solutions of OC is shown in Figure 14. An excellent straight line is obtained over the concentration range 4-200 m$\underline{M}$ with unity intercept in agreement with equation II. The value of $\alpha = 33\ \underline{M}^{-1}$, obtained by squaring the value of the slope, suggests that OC is a very efficient electron scavenger. This result is in agreement with results of the EPR study which shows that electron capture is the precursor of the cage radical as discussed in an earlier section of this report.

The results for EOC are also shown in Figure 14. The slope of the best line through the experimental points for EOC is the

Figure 14. Schuler plots for OC and EOC.



same as for OC leading to an $\alpha = 33\ \underline{M}^{-1}$ and indicating that electron capture by the carborane cage is not affected by substitution of an ethyl group for a hydrogen at the cage carbon. The intercept of the ordinate is 0.8 instead of unity as required by equation II, however. This unusual behavior has not been observed for any common electron scavengers[17] and cannot be explained either by a systematic experimental error or by adjustment of the approximate $\underline{G}$ values, 1.8 or 3.9. If the equation for the observed line for EOC is rewritten in the form of equation I, equation III is obtained.

$$\underline{G}(H_2) = 1.8 + 3.9\left[1 - \frac{[(\alpha S)^{\frac{1}{2}} - 0.2]}{1+[(\alpha S)^{\frac{1}{2}} - 0.2]}\right] \qquad \text{(III)}$$

The meaning, if any, of this equation is unclear at this time. At any carborane concentration, the yield of hydrogen from cyclohexane solutions of EOC is greater than that from OC as can be seen by comparison of Figure 10 and 11 although the identical $\alpha$ values suggest both OC and EOC capture electrons with equal efficiency. Intuitively, then, the higher yields of hydrogen are caused either by hydrogen formation from EOC (but not OC) following electron capture or by some other hydrogen-forming process of EOC (but not OC). The first alternative is unlikely because an electron-capture precursor of such a hydrogen-forming process would require that the reaction rate for the process be dependent upon EOC concentration in the same range as the rate for electron-capture, i.e., the straight line for EOC in Figure 14 is inconsistent with the first alternative. Energy transfer from directly excited cyclohexane to the carboranes followed by atomic or molecular hydrogen production from excited EOC only (i.e., from the ethyl substituent)

satisfies the requirements of the second alternative. Such energy transfer, however, would have to be complete at 4 m$\underline{M}$ to be concentration independent. Even if Forester energy transfer with a specific rate of about $5 \times 10^{10}$ $\underline{M}^{-1}$ $sec^{-1}$ is invoked, a lifetime of the lowest cyclohexane excited state of 0.5 nsec[19,20] allows only about 10% energy transfer at 4 m$\underline{M}$. Moreover, the absorption spectrum of EOC does not overlap the cyclohexane emission as discussed in a later section of this report. Therefore, at the present time there is no satisfactory explanation of equation III.

Application of equation II to values of $\underline{G}(H_2)$ found for VOC and AOC in cyclohexane is shown by Figure 15. The points for VOC below 10 m$\underline{M}$ lie on a straight line through unity and a value of $\alpha = 10.6$ $\underline{M}^{-1}$ is obtained from the slope. This $\alpha$ value, although still characteristic of a moderately good electron scavenger, is one third of the $\alpha$ value for OC and EOC. It is tempting to speculate that the inductive and/or resonance effect[7] of the carborane cage on the $\pi$ electrons of the double bond may cause a decreased affinity of the cage for electrons and, thus, a lower $\alpha$ value.

The concave upward curvature above 10 m$\underline{M}$ is caused by lower values of $\underline{G}(H_2)$ than would be predicted by electron scavenging alone. Hydrogen atom scavenging by the double bond can explain this curvature. If a competition exists as shown in reactions 1 and 2 between hydrogen addition to the double bond and hydrogen abstraction from cyclohexane (or from the carborane cage with approximately the same specific rate), then equation I must be modified to the

$$H\cdot + \theta CH = CH_2 \rightarrow \theta(CH_3)CH\cdot \qquad 1$$

$$H\cdot + C_6H_{12} \rightarrow H_2 + C_6H_{11}^{\cdot} \qquad 2$$

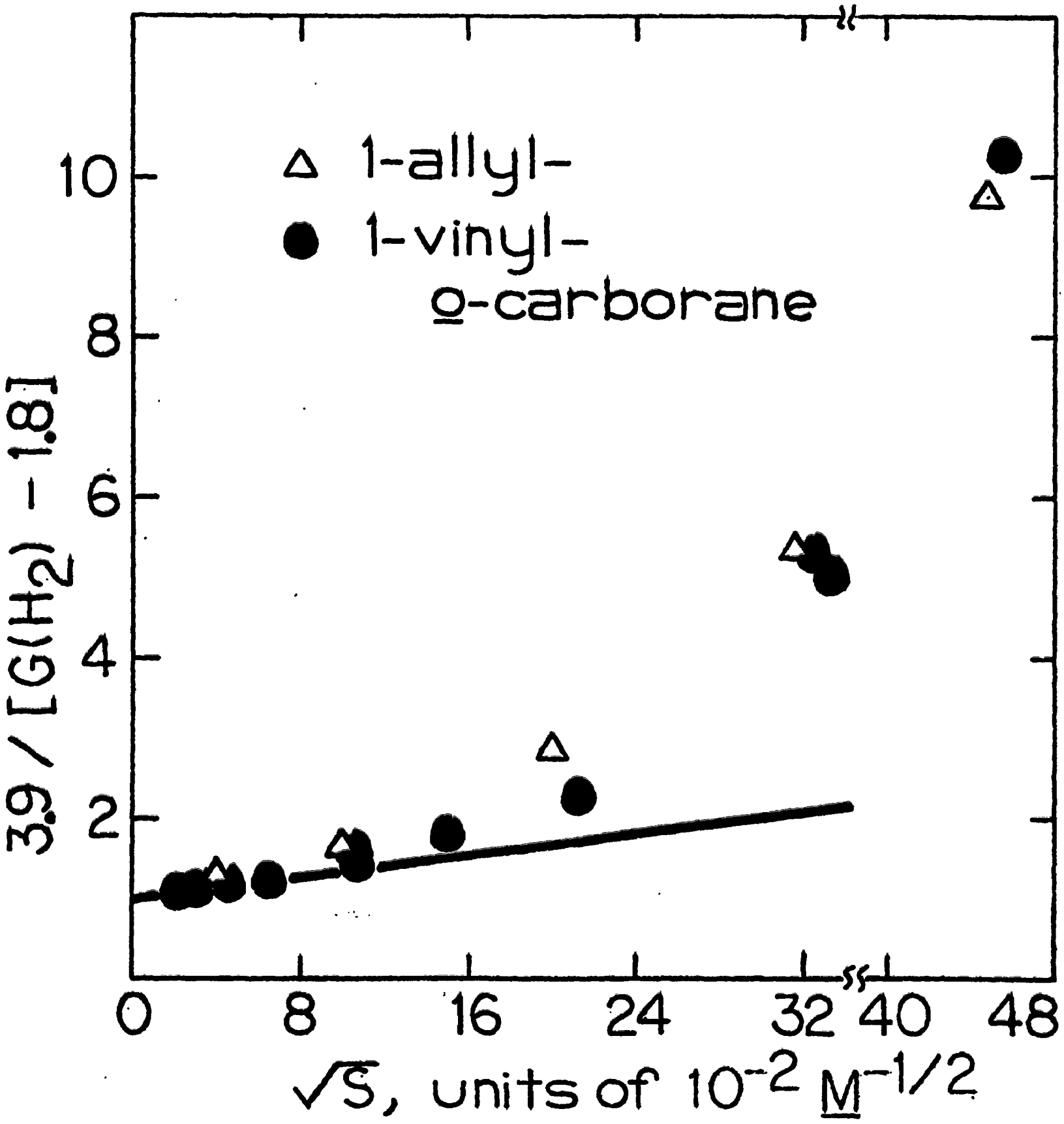



Figure 15. Schuler plots for VOC and AOC.

form shown in equation IV.

$$\underline{G}(H_2) = \left[ 3.0 + 0.9\left(\frac{\underline{k}_2[RH]}{\underline{k}_1[S]+\underline{k}_2[RH]}\right)\right] \ast$$

$$\left[ 1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right] +$$

$$1.2 + 0.6 \left[\frac{\underline{k}_2[RH]}{\underline{k}_1[S]+\underline{k}_2[RH]}\right] \qquad \text{(IV)}$$

The $\underline{G}$-value coefficient of the first term of equation I must be separated in equation IV into the $\underline{G}(H_2) = 3$ of molecular hydrogen and the $\underline{G}(H_2) = 0.9$ of hydrogen with an atomic hydrogen precursor;[16] the yield of 0.9 is multiplied by the fraction of the hydrogen atoms which abstract hydrogen from the solvent (or the carborane cage) rather than add to the double bond of the VOC or AOC solute, S. Similarly the $\underline{G}$-value of 1.8 of non-ionicly produced hydrogen must be divided into a $\underline{G}(H_2) = 1.2$ of molecular hydrogen and a $\underline{G}(H_2) = 0.6$ of hydrogen with an atomic hydrogen precursor;[16] the latter is multiplied by the fraction which abstract. This equation thus accounts for loss of molecular hydrogen by capture of either electron or atomic hydrogen precursors.

In the limit as $[S] < 10m\underline{M}$, equation IV approaches equation I (This will be justified later.) and, therefore, the value of $\alpha = 10.6\ \underline{M}^{-1}$ can be legitimately obtained from the limiting slope in Figure 15. With this $\alpha$ value and the value of $\underline{k}_2/\underline{k}_1$, values of $\underline{G}(H_2)$ calculated with equation IV may be compared with experimental values as shown by the solid line in Figure 12. For the purposes of this calculation, the value of $\underline{k}_1$ for VOC is assumed not to

differ significantly from that for ethylene for which the value of $\underline{k}_2/\underline{k}_1 = 0.004$ has been obtained.[17] The agreement between values of calculated $\underline{G}(H_2)$ and measured $\underline{G}(H_2)$ is seen to improve if results from equation IV are compared to those from equation I shown by the dashed line in Figure 12. Variation of the value of $\underline{k}_2/\underline{k}_1$ used in equation IV does not improve the overall agreement, i.e., over the entire concentration range.

The calculated values of $\underline{G}(H_2)$ for cyclohexane solutions of AOC are also compared with measured values in Figure 13. The value of $\alpha = 10.6\ \underline{M}^{-1}$ found for VOC was used and a value of $\underline{k}_2/\underline{k}_1 = 0.002$ was found to give the best overall fit to the data. The factor of two difference between values of $\underline{k}_2/\underline{k}_1$ for VOC and AOC can be attributed to a larger $\underline{k}_1$ for AOC than for VOC. This difference is explained by the reduction of the electron-withdrawing effect of the carborane cage on the double bond caused by the insulating methyl group of AOC. Radical addition to the allyl double bond is therefore faster than to the vinyl double bond.[7,21] These values of $\underline{k}_2/\underline{k}_1$, although of the expected magnitude,[17] are only approximate and therefore conclusions drawn from them should be viewed cautiously. Nevertheless, the values obtained justify the use of the limiting slope in Figure 15 to obtain $\alpha$ for VOC. For [VOC] $\leq 4 m\underline{M}$ (the highest concentration used to obtain $\alpha$) the value of $\underline{G}(H_2)$ is reduced by less than 2.5% by hydrogen atom scavenging compared to a reduction of 10% in $\underline{G}(H_2)$ owing to electron scavenging by 4 $m\underline{M}$ VOC. The fair agreement of the calculated and the measured values of $\underline{G}(H_2)$ at low VOC and AOC concentration also supports the validity of $\alpha = 10.6\ \underline{M}^{-1}$ for VOC and AOC. Furthermore, variation of these values of $\alpha$ or $\underline{k}_2/\underline{k}_1$ did not significantly

improve the fit to the data.

The calculated values of $\underline{G}(H_2)$ above a solute concentration of 10 m$\underline{M}$ are systematically higher than measured values of $\underline{G}(H_2)$ although hydrogen atom scavenging has been included in equation IV. The source of this discrepancy could not be attributed to a systematic error in the value of one of the experimental constants in equation IV. The failure to obtain complete agreement is not surprising, however, considering that no allowance was included in equation IV for quenching of electronically excited cyclohexane. Cyclohexane, either directly excited or excited $\underline{via}$ electron-cation recombination of unscavenged electrons, may yield hydrogen and, as shown in a later section of this report, both VOC and AOC are capable of accepting excitation energy from cyclohexane. In contrast, both OC and EOC are inefficient energy acceptors from excited cyclohexane, as shown later, and therefore Figure 14 is a straight line for solute concentration in the range 1-200 m$\underline{M}$. Although the calculated values of $\underline{G}(H_2)$ could be adjusted further by including Stern-Volmer quenching kinetics in equation IV, the value of the product of $\underline{k}_q$, the specific rate of energy transfer, and $\tau$, the lifetime of the excited state of cyclohexane in the absence of quencher, is probably not meaningful owing to accumulation of errors in the calculation and the uncertainty in measured $\underline{G}(H_2)$. Approximate values of $\underline{k}_q\tau$, however, are in the range of observed values.[19,20,22]

In summary, the hydrogen yields suggest that the carborane cage is an efficient electron scavenger, but electron donating substituents such as vinyl appear to decrease the efficiency of electron scavenging by the cage. The ethyl substituent appears

to be involved in an ill-defined hydrogen-forming reaction, but the carborane cage of EOC is an efficient scavenger. The vinyl and allyl substituents of VOC and AOC react with hydrogen atoms with a specific rate similar to that for ethylene; AOC may even be somewhat faster owing to a reduction of the electron-withdrawing effect of the carborane cage on the double bond by methylene. Furthermore, energy transfer from excited cyclohexane to VOC and AOC would explain the measured values of $\underline{G}(H_2)$ over the entire concentration range. This last observation will be discussed further in the section on the absorption spectra of the carboranes.

The results of the hydrogen yield study thus suggest that the rate of formation of the radical, $\theta(CH_3)CH\cdot$, in cyclohexane is comparable to that for ethylene. Because no measurable loss of monomer occurred from VOC or AOC solutions and no polymer was observed by gel permeation chromatography of concentrates from such solutions, the reaction of the radical, $\theta(CH_3)CH\cdot$, does not appear to include addition to double bonds owing perhaps to a combination of radical stabilization by the electron-withdrawing influence of the carborane cage[7,21] and steric inhibition. The former of these two probably predominates. For the concentrated solutions used in the polymerization study reported in a previous section and by Wright and Klingen,[13] formation of $\theta(CH_3)CH\cdot$ was probably inhibited by the efficient capture of electrons and perhaps excited states; both are atomic hydrogen precursors. Electron capture is the precursor of the cage radical and thus mainly cage dimers were found in the product. Reactions of $\theta(CH_3)CH\cdot$ will be discussed further in the next section.

Yields of Products Other Than $H_2$-- The yields of cyclohexene, $C_6H_{10}$, and dicyclohexyl, $C_{12}H_{22}$, were measured to help elucidate the mechanism of radical reactions in cyclohexane solutions of the carboranes. Both $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$ are reduced by the presence of the carboranes as shown by Figures 10 to 13. This reduction is expected if two conditions are fulfilled. The first is that electrons are captured by the carborane solute; this condition is fulfilled as has been shown from analysis of the hydrogen yields. The second condition is that during ion recombination solute anions do not decompose into one or more radicals which are able to abstract hydrogen from cyclohexane solvent and thus create one or more cyclohexyl radicals, $C_6H_{11}\cdot$, for each electron scavenged. If this happens, the yields of $C_6H_{10}$ and $C_{12}H_{22}$ from precursor $C_6H_{11}\cdot$ do not reflect a simple dependence on the concentration of electron scavenger. The yields might even increase with concentration as is found for the electron scavenger, $N_2O$.[16,23] Thus, the fact that the yield of $C_6H_{10}$ and $C_{12}H_{22}$ are both reduced for the carboranes suggests that ion recombination of a carborane anion and the cation of either the solvent or the solute does not result in formation of radicals capable of hydrogen abstraction from cyclohexane. This does not exclude the formation of the cage radical or perhaps the alkyl substituent radical because as argued earlier these are incapable of hydrogen abstraction from alkanes.

If no reaction other than reactions 3 and 4 removes cyclohexyl radicals, the dependence of $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$ on carborane concentration is caused by a concentration-dependent $\underline{G}(C_6H_{11}\cdot)$. The dependence of $\underline{G}(C_6H_{11}\cdot)$ on carborane concentration is itself

caused by scavenging of cyclohexyl radical precursors, the electron and, in the case of VOC and AOC, the hydrogen atom.

$$C_6H_{11}\cdot + C_6H_{11}\cdot \rightarrow C_6H_{10} + C_6H_{12} \qquad 3$$

$$C_6H_{11}\cdot + C_6H_{11}\cdot \rightarrow C_{12}H_{22} \qquad 4$$

The value of $\underline{G}(C_6H_{10})$ for both OC and EOC can be calculated from equation VII if only electron capture is assumed to be important. The value of $\alpha$ is $33\underline{M}^{-1}$ as found from the hydrogen yield study and the value of $\underline{k}_3/\underline{k}_4 = 1.1$ was found by Cramer.[24] Equations V and VI are obtained from the set of reactions and $\underline{G}$-values assigned by Bansal and Schuler[16] for cyclohexane radiolysis which are shown in reactions 5 to 11. The factor, 2.7/3.9, is used to normalize the yields observed in the present work to those found by Bansal and Schuler,[16] *i.e.*, a value of $\underline{G}(C_6H_{10}) = 2.7$ is found for pure

$$\underline{G}(C_6H_{11}\cdot) = 3.9\left[1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right] + 1.8 \qquad V$$

$$\underline{G}(C_6H_{10}) = \frac{2.7}{3.9}\left[\frac{\underline{k}_3}{\underline{k}_3+\underline{k}_4} \cdot \frac{\underline{G}(C_6H_{11}\cdot)}{2} + 1.55\left(1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right) + 0.87\right] \qquad VI$$

$$\underline{G}(C_6H_{10}) = \frac{2.7}{3.9}\left[\frac{2.57}{1+(\alpha S)^{\frac{1}{2}}} + 1.34\right] \qquad VII$$

cyclohexane in the present work but reactions 5 to 11 would predict a value of $\underline{G}(C_6H_{10}) = 3.9$. The solid curves with ordinate intercepts at $\underline{G}(C_6H_{10}) = 2.7$ in Figures 10 and 11 are the predicted yields of cyclohexene from equation VII. Before discussing the implications

of the lack of agreement between the theoretical and observed yields, the same kinetics will be applied to dicyclohexyl

| Ionic Reactions | G-value | |
|---|---|---|
| $C_6H_{12}^+ + e \rightarrow C_6H_{11}\cdot + H\cdot$ | 0.89 | 5 |
| $C_6H_{12}^+ + e + C_6H_{12} \rightarrow 2C_6H_{11}\cdot + H_2$ | 1.06 | 6 |
| $C_6H_{12}^+ + e \rightarrow C_6H_{10} + H_2$ | 1.55 | 7 |
| $C_6H_{12}^+ + e + C_6H_{12} \rightarrow C_{12}H_{22} + H_2$ | 0.40 | 8 |
| **Non-ionic Reactions** | | |
| $C_6H_{12} \rightarrow C_6H_{10} + H_2$ | 0.87 | 9 |
| $C_6H_{12} \rightarrow C_6H_{11}\cdot + H\cdot$ | 0.57 | 10 |
| $2C_6H_{12} \rightarrow 2C_6H_{11}\cdot + H_2$ | 0.33 | 11 |

The value of $\underline{G}(C_{12}H_{22})$ can be calculated for OC and EOC using the same assumption incorporated in the calculation of $\underline{G}(C_6H_{10})$, *i.e.*, electron scavenging is solely responsible for yield reduction. Equation VIII is obtained by reference to reactions 5 to 11.

$$\underline{G}(C_{12}H_{22}) = \frac{1.50}{1.76}\left[\frac{\underline{k}_4}{\underline{k}_3+\underline{k}_4}\,\frac{\underline{G}(C_6H_{11}\cdot)}{2} + 0.40\left(1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right)\right] \qquad \text{VIII}$$

Values of $\alpha = 33\underline{M}^{-1}$ and $\underline{k}_3/\underline{k}_4 = 1.1$ are the same. The factor, 1.50/1.76, normalizes the calculated yield to that measured in this work from pure cyclohexane as discussed earlier for cyclohexene yields. Equation IX results from simplification of equation VIII using equation V.

$$\underline{G}(C_{12}H_{22}) = \frac{1.50}{1.70}\left[\frac{1.33}{1+(\alpha S)^{\frac{1}{2}}} + 0.48\right] \qquad \text{IX}$$

The solid curves with intercepts at $\underline{G}(C_{12}H_{22}) = 1.5$ in Figures 10 and 11 are predicted by equation IX. The agreement between predicted and measured values is seen to be reasonably good for both OC and EOC, thereby arguing for the validity of the initial assumptions, i.e., only electron scavenging by the carboranes occurs and cyclohexyl radicals disappear only by reactions 3 and 4. The predicted curves for $\underline{G}(C_6H_{10})$ however do not agree well with the measured values. The measured values for OC depart from theoretical values by about 0.5 G-units from 20 to 200 mM. The difference in such values for EOC is not as much as for OC, but also requires explanation. It may be argued that any agreement between predicted and measured values is fortuitous, considering the approximations implicit in the derivations of equations VII and IX. An alternative explanation is that the carborane interferes with a cyclohexene-forming reaction not involving a cyclohexyl radical precursor. Reaction 9 is such a reaction. The formation of molecular hydrogen has been showen to occur at least partially by reaction 12

$$C_6H_{12}^{*} \rightarrow (C_6H_{11}\cdot + H\cdot) \rightarrow C_6H_{10} + H_2 \qquad 12$$

where the radicals in parentheses represents the cyclohexyl radical and sibling hydrogen atom in a solvent cage.[25,26] Reaction 7 may also involve a similar intermediate step. If the sibling hydrogen atom abstracts hydrogen rapidly from carborane, the radical pair is converted into a cyclohexyl radical and a carboranyl cage radical; the probability of coupling for the new cage pair is unchanged. The yield of hydrogen from reaction 12 is not affected by this mechanism, but cyclohexene yield is decreased. Comparison of the

difference between predicted and theoretical values for EOC and OC suggests that EOC is less efficient than OC in such a hydrogen displacement reaction. Perhaps the strong electron-withdrawing tendency of the carborane cage causes the reactivity of cage hydrogens in OC and this reactivity is somewhat lower in EOC owing to electron-induction from the ethyl group. Such an explanation suggests that the hydrogen bonded to the cage carbon is the reactive hydrogen, because the carbon end of the cage is electron deficient.[7]

The proposed hydrogen displacement reaction within the solvent cage will be tested by identifying and measuring cyclohexyl adducts of OC and EOC in the irradiated cyclohexane solutions. Confirmation of such a reaction would support the proposed mechanism and would suggest that atomic hydrogen abstracts hydrogen from OC and EOC rapidly. In contrast, hydrogen abstraction from OC and EOC by the cyclohexyl radical is slow because all the cyclohexyl radicals formed are accounted for by reactions 3 and 4.

The last conclusion is in agreement with results from EPR studies which indicate that cage radical is present immediately following radiolysis at 77°K, presumably owing to hydrogen abstraction by atomic hydrogen. Warming of the alkane glass matrix allows the solvent radicals to disappear without an increase in cage radical. Thus both the alkyl radicals formed in the glass and the cyclohexyl radicals formed in cyclohexane at 31° abstract hydrogen from the carborane cage too slowly to compete with other radical-eliminating reactions.

The values of $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$ for VOC and AOC may also be calculated. However, the added complication of hydrogen atom

and cyclohexyl radical scavenging by the double bond must be considered. Qualitatively, these added reactions are seen in Figures 12 and 13 as a much larger decrease in $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$ for VOC and AOC compared to that observed in Figures 10 and 11 for OC and EOC at the same concentration. Equations X to XII can be used to calculate $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$ for VOC and AOC.

$$\underline{G}(C_6H_{11}\cdot) = 3.01\left[1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right] + 0.89\left[1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right]\left[\frac{\underline{k}_2[RH]}{\underline{k}_1[S]+\underline{k}_2[RH]}\right] + 0.57\left[\frac{\underline{k}_2[RH]}{\underline{k}_1[S]+\underline{k}_2[RH]}\right] + 1.23 \qquad X$$

$$\underline{G}(C_6H_{10}) = \frac{2.7}{3.9}\left[\frac{\underline{k}_3}{\underline{k}_3+\underline{k}_4}\cdot\frac{\underline{G}(C_6H_{11}\cdot)}{2} + 1.55\left(1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right) + 0.87\right] \qquad XI$$

$$\underline{G}(C_{12}H_{22}) = \frac{1.5}{1.7}\left[\frac{\underline{k}_4}{\underline{k}_3+\underline{k}_4}\cdot\frac{\underline{G}(C_6H_{11}\cdot)}{2} + 0.40\left(1 - \frac{(\alpha S)^{\frac{1}{2}}}{1+(\alpha S)^{\frac{1}{2}}}\right)\right] \qquad XII$$

From the study of hydrogen yields, $\alpha = 10.6\ \underline{M}^{-1}$ for both VOC and AOC. The value for $\underline{k}_1/\underline{k}_2 = 0.004$ is used for VOC and $\underline{k}_1/\underline{k}_2 = 0.002$ is

used for AOC. Also $\underline{k_3}/\underline{k_4}$ = 1.1 as previously discussed.[24] Normalizing factors are used as explained earlier for equations VII and IX. Equations XI and XII include electron and hydrogen atom scavenging, but because nothing is known about cyclohexyl radical scavenging in such a system, no scavenging kinetics for such a reaction is included in these equations. Therefore, equations XI and XII do not give a satisfactory theoretical curve for plotting in Figure 12 and 13 similar to those shown in Figures 10 and 11 obtained by use of equations VII and IX. Representative values of $\underline{G}(C_6H_{10})$ and $G(C_{12}H_{22})$ have been calculated from equations XI and XII, however, and are compared in Table II with experimental values at the same VOC and AOC concentrations.

The large differences between calculated and measured values in Table II shows the importance of cyclohexyl radical reactions with VOC and AOC. Closer examination of Table II shows that these differences between measured and calculated values of $\underline{G}(C_6H_{10})$ and $\underline{G}(C_{12}H_{22})$, $\underline{i.e.}$, $\Delta\underline{G}(C_6H_{10})$ and $\Delta\underline{G}(C_{12}H_{22})$, are constant above about 10 $\underline{mM}$ VOC or AOC. The average value of $\Delta\underline{G}(C_6H_{10})$ for VOC and AOC is 0.94 and 0.90, respectively. Similiarly, $\Delta\underline{G}(C_{12}H_{22})$ for VOC and AOC is 0.60 and 0.53. The difference between values of $\Delta\underline{G}(C_6H_{10})$ and $\Delta\underline{G}(C_{12}H_{22})$ for VOC and AOC are not statistically significant. Therefore, $\Delta\underline{G}(C_6H_{10}) \cong 0.92$ and $\Delta\underline{G}(C_{12}H_{22}) \cong 0.56$. A value of the yield of cyclohexyl radicals which have reacted with VOC or AOC in competition with reaction 3 and 4 is calculated from $\Delta\underline{G}(C_{12}H_{22})$ to be $\underline{G}(C_6H_{11}\cdot) = 2.35$. The value of $\underline{G}(C_6H_{11}\cdot)$ calculated from $\Delta\underline{G}(C_6H_{10})$ is 3.51. The difference between these values, 1.16, suggests that a yield of cyclohexene of 0.30 was quenched independent

TABLE II

| [S] mM | G($C_8H_{10}$) Calculated | G($C_8H_{10}$) Measured | G($C_{12}H_{22}$) Calculated | G($C_{12}H_{22}$) Measured |
|---|---|---|---|---|
| | | 1-vinyl-o-carborane | | |
| 0.45 | 2.60 | 2.32 | 1.41 | 1.26 |
| 0.90 | 2.55 | 2.26 | 1.38 | 1.02 |
| 4.12 | 2.39 | 1.70 | 1.27 | 0.55 |
| 11.3 | 2.20 | 1.29 | 1.14 | 0.40 |
| 44.8 | 1.87 | 0.85 | 0.91 | 0.29 |
| 104.2 | 1.66 | 0.73 | 0.77 | 0.22 |
| 208.5 | 1.50 | 0.59 | 0.66 | 0.16 |
| | | 1-allyl-o-carborane | | |
| 4.0 | 2.36 | 2.04 | 1.25 | 0.92 |
| 10.0 | 2.20 | 1.40 | 1.13 | 0.60 |
| 40.7 | 1.88 | 1.03 | 0.90 | 0.29 |
| 100.0 | 1.64 | 0.67 | 0.75 | 0.23 |
| 200.0 | 1.50 | 0.54 | 0.65 | 0.19 |

of a cyclohexyl precursor. A similar observation for OC and EOC was discussed earlier and assigned to quenching of reactions such as reaction 12. The value of 0.3 found for VOC and AOC is close to the value of about 0.2 found for EOC and is not too different from the value of 0.5 found for OC. The previous explanation for OC and EOC can be extended to cyclohexane solutions of VOC and AOC. However, in this latter system hydrogen addition to VOC and AOC would predominate over abstraction from the carborane cage and the sibling cyclohexyl radical in the solvent cage would add. Such a mechanism would lead to a decrease in $\underline{G}(H_2)$ as well as $\underline{G}(C_6H_{10})$ by about 0.3. Examination of Figure 12 and 13 shows that the experimental hydrogen yields fall about 0.3 G-units below those predicted for both VOC and AOC. Thus, the quenching of reaction 12 can be identified with the "excited state" suggested earlier as an explanation for the difference between observed and experimental hydrogen yields.

The cyclohexyl radical scavenging reaction is complete for concentration of VOC or AOC above 10 m$\underline{M}$ as shown by the constant difference between calculated and measured values. The concentration independence is consistent with a relatively long lifetime for the cyclohexyl radical because at the dose rate of about $3.6 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$ and with both electron and hydrogen atom scavenging, the steady-state cyclohexyl radical concentration is quite low and bimolecular radical reactions 3 and 4 do not compete readily. The yields of $C_6H_{10}$ and $C_{12}H_{22}$ for VOC and AOC concentration greater than 10 m$\underline{M}$ are mainly produced by reactions 7,8, and 9 which do not involve a cyclohexyl radical (except perhaps as an intermediate in the solvent cage[25]).

The value of $\underline{G}(C_6H_{11}\cdot) = 2.35$ estimated for the yield of cyclohexyl radicals which are scavenged by VOC and AOC suggests that addition products with this $\underline{G}$-value should be found in the irradiated cyclohexane solutions. Two products are observed by gas chromatography and estimated yields are shown in Table I. The agreement of the sum of these values and the value 2.35 is excellent for VOC; that for AOC is not as good. The experimental difficulty of accurate quantitative measurements of the high column temperature required may explain some of the error. The yields of these products is concentration independent in the same concentration range as observed for $\underline{G}(C_6H_{11}\cdot) = 2.35$. Mass spectrometric analysis of a portion of the cyclohexyl adduct, which was obtained by preparative ALC, identified the peaks as cyclohexyl adducts to VOC. The fact that two poorly resolved peaks were observed by gas chromatography may indicate that one of these peaks corresponds to an unsaturated cyclohexyl adduct, i.e., the cyclohexyl adduct undergoes disproportionation rather than coupling. The observation of cyclohexyl adducts to VOC in cyclohexane is not in conflict with failure to find such products in the work of Wright and Klingen[13] because as is now obvious the high VOC concentration used in that work precluded formation of cyclohexyl radicals via ionic processes or excited states.

In summary, the arguments based on yields of cyclohexene, dicyclohexyl and the cyclohexyl adducts of the carboranes support interpretation of the hydrogen yields. Although somewhat approximate, such arguments give a semiquantitative description of carborane radiolysis in cyclohexane. The evidence for the following

conclusions appears to be especially convincing.

1. Electron capture by carboranes is very efficient.
2. Both hydrogen atoms and cyclohexyl radicals add rapidly to the double bonds of VOC and AOC. (No mention has been made of hydrogen abstraction from the methylene carbon of AOC. If it occurs, it is not evident in these data.)
3. Cyclohexyl adduct radicals with VOC and AOC do not initiate addition polymerization, but instead appear to disproportionate, owing perhaps to steric inhibition.
4. Hydrogen atom adduct radicals such as $\theta(CH_3)CH\cdot$ are apparently very stable, owing to the electron withdrawing effect. Such radicals in solution probably couple. They are unable to compete with VOC for hydrogen atoms. The adduct radical, $\theta(CH_3)CH\cdot$, apparently is too stable to add rapidly to the double bond of VOC and therefore polymers are not formed.

## Ultraviolet Absorption Spectra of the Carboranes

During the study of γ-irradiated cyclohexane containing carborane solutes, energy transfer from electronically excited cyclohexane to the carboranes was suggested to partially explain the large decrease in hydrogen yields. Therefore, a study of the excited states of the carboranes was conducted to determine if such energy transfer is possible. Spectrofluorimetric study of the carboranes as solutes in cyclohexane showed that an emission spectrum common to all the carboranes is observed if light is absorbed by the carboranes in the absorption peak near 270 nm.[5] This suggested that this weak absorption peak is caused by an impurity and subsequently the peak was eliminated by a revised technique of carborane purification. The remaining strong absorption peak of shorter wavelength was not affected by the purification steps taken to remove the peak near 270 nm. Photo-excitation of the carboranes with absorption in the short wavelength peak was not possible with available equipment so that fluorescence from photo-excited carboranes has not been examined further.

The absorption spectra of the carboranes shown in Table III have been remeasured in cyclohexane at 23° on a Cary 17 spectrometer. Peak maxima were observed only for the carboranes with unsaturated substituents and all obeyed Beer's law. Because the weak absorption of ethylene at 200 nm is known to be both shifted and enhanced by substituents,[26] the absorption peak at 194 nm for VOC could be assigned to ethylene absorption with a hypsochromic shift caused by the acidic, electron-withdrawing carborane cage. This explanation of the VOC absorption does not agree however with the observation

TABLE III

Ultraviolet Absorption of Carboranes

| Compound | $\lambda_{max}$ nm | $\epsilon_{max}$ $M^{-1}cm^{-1}$ | $\epsilon_{201}$ $M^{-1}cm^{-1}$ | $\int_0^\infty f(\nu)\epsilon(\nu)d\nu$ ** |
|---|---|---|---|---|
| OC | < 185 | 270* | 20 | ~ 0.02 |
| EOC | < 185 | 100* | 34 | ~ 0.02 |
| IPrOC† | < 185 | 500* | 143 | |
| VOC | 194 | 10,600 | 8,800 | 1.00 |
| AOC | ~ 185 | 2,700 | 125 | 0.24 |
| IPOC† | 203 | 9,000 | 8,800 | |

* Measured at 190 nm.

** Estimated spectral overlap of cyclohexane emission spectrum with carborane absorption spectra relative to unity for 1-vinyl-o-carborane.

† IPrOC is 1-isopropyl-OC; IPOC is 1-isopropenyl-OC.

that the absorption peak for AOC lies even further into the ultraviolet than does that of VOC. If the double bond is the chromophore, removal of the carborane substituent by one methylene group should have caused a bathochromic shift rather than the observed hypsochromic shift relative to the 200-nm ethylene absorption. The inductive effect of the carborane cage on the double bond should have decreased owing to the increase in separation of the double bond from the cage. Also, hyperconjugation of the methylene hydrogens should produce a bathochromic shift.

An alternative explanation for the absorption spectra which is consistent with all the data is that the absorption is centered in the carborane cage. The presence of substituents affect the absorption by their positive inductive effect as well as a resonance effect on the cage, both causing bathochromic shifts. The effect of the vinyl substituent in VOC is to shift the absorption from less than 185 nm to 194 nm, a strong bathochromic shift consistent with both a positive inductive effect and a resonance effect. The resonance effect however is decreased in AOC owing to the methylene group and therefore the bathochromic shift is also reduced. For 1-isopropenyl-o-carborane, the bathochromic shift is increased by the methyl group. Hyperconjugation of the methyl group usually causes a 5-nm bathochromic shift in conjugated polyenes.[27] Perhaps the inductive effect also adds to the 9-nm shift observed for 1-isopropenyl-o-carborane relative to VOC. This large shift and the large shift of the absorption of VOC relative to OC also strongly suggests that a resonance effect involving the cage electrons must be operating. No other strong evidence for such resonance has been

found to date by other workers.[28] The inductive effect must also influence the oscillator strength as shown by the smaller extinction coefficient for AOC relative to VOC or 1-isopropenyl-o-carborane. The inductive effect would be less for AOC, again owing to the separation of the polarizable π electrons from the carborane cage by the methylene group. Finally, it is tempting to predict that the maximum of the absorption spectrum for OC will be found at about 164 nm based on the bathochromic shift of 30 nm usually estimated for a double bond.[27] The maxima for EOC should be found at about 170 nm and for 1-isopropyl-o-carborane, at about 174 nm.

The last two columns in Table III show the extinction coefficient for each carborane at the maximum of the cyclohexane fluorescence spectrum[22] and the value of the overlap integral normalized to unity for VOC. The table shows that efficient energy transfer is allowed from cyclohexane to VOC and AOC, but not to OC and EOC. This observation has relevance to the earlier discussion of hydrogen yields in cyclohexane radiolysis.

## Radiolysis of 1-Allyl-o-Carborane

Establishment of the melting point-- The melting point of AOC has been reported to be in the range 63-65°.[29] However, the melting point of the purified AOC used in this study was found by differential thermal analysis to be about -3°. A possible explanation for such a discrepancy is that the AOC used in this study was contaminated with impurities causing a melting point depression. To eliminate this possibility, quantities of AOC were purified by preparative gas chromatography. Portions of this purified AOC were found to melt at -3°. The mass spectrum of this purified AOC was obtained with a duPont Model 21-492 GC-MS and shows a single fragmentation pattern characteristic of AOC. Assignment of the bands in the infrared and the proton NMR spectrums, Tables IV and V, of the purified material is consistent with the structure expected for pure AOC. Therefore, it must be concluded that the melting point of AOC is -3° and that the value found by Heying and co-workers[29] was incorrect, perhaps owing to contamination with OC. Such a mixture would have a melting point intermediate between that of OC at 295° and that of AOC at -3°. The main impurity of commercially available AOC is OC and careful purification is required to eliminate it from AOC.

Radiolysis of pure AOC-- Values of $G(-m)$ and per cent conversion of monomer to products were measured at 31° for doses in the range $(0.9\text{-}7.5) \times 10^{21}$ eV $g^{-1}$ with a dose rate of $3.9 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$. Results are shown in Figure 16. The main product of radiolysis was an oligomeric solid which was precipitated from an n-hexane solution

TABLE IV

Infrared Absorptions of 1-Allyl-o-Carborane
and Its Radiolysis Oligomer

| λ(microns) | Intensity* | | Assignment |
|---|---|---|---|
| | AOC | Oligomer | |
| 3.12 | absent | w,b | |
| 3.27 | m,sh | m,sh | C-H stretch polyhedron $-CH{=}CH_2$ |
| 3.35 | w,sh | absent | C-H stretch $-CH_2$ |
| 3.42 | w,b | w,vb | C-H stretch $-CH_2$ |
| 3.88 | vs,b | vs,b | B-H stretch polyhedron |
| 5.40 | w,vb | absent | |
| 6.12 | w,sh | absent | -C=C stretch |
| 7.00 | m,sh | m,b | C-H bend $-CH_2$ |
| 7.09 | m,sh | absent | C-H bend $-CH{=}CH_2$ |
| 7.64 | w,sh | absent | C-H bend $-CH{=}CH_2$ |
| 7.78 | w,sh | absent | C-H bend $-CH{=}CH_2$ |
| 8.33 | w,b | absent | C-H bend |
| 9.08 | m,b | w,b | C-H bend |
| 9.42 | m,sh | w,b | C-H bend |
| 9.90 | s,sh | w,b | C-H bend |
| 10.12 | s,sh | w,b | C-H bend |
| 10.80 | s,sh | w,b | C-H bend |
| 12.82 | w,b | absent | C-H bend |
| 14.00 | s,sh | s,sh | C-H bend $-CH_2$ $B_{10}C_2$ polyhedron |
| 14.40 | w,sh | absent | C-H rock |
| 14.90 | w,b | absent | C-H rock |

* vs = very strong, s = strong, m = medium,
w = weak, sh = sharp, b = broad.

TABLE V

Proton NMR Spectrum of 1-Allyl-o-Carboranes*
and Its Radiolysis Oligomer.*

| δ,ppm | Δν,$H_z$ | Character | Assignment |
|---|---|---|---|
| | | 1-Allyl-o-Carborane | |
| 2.90 | 3 | sharp doublet | allyl -$CH_2$ |
| 3.56 | none | broad singlet | polyhedron C-H |
| 5.42 | | sharp multiplets | vinyl protons |
| | | Oligomer | |
| 0.60 | none | broad singlet | |
| 1.39 | none | broad singlet | |
| 3.52 | none | broad singlet | polyhedron C-H |

* Spectra were obtained in $CDCl_3$ with an external TMS reference.

of the radiosylate. The number average molecular weight, $\overline{M}n$, of the oligomers was obtained by vapor pressure osmometry and used to calculate $\overline{DP}_n$ which is $\overline{M}_n$ divided by the monomer molecular weight, i.e., $\overline{DP}_n$ is the number average degree of polymerization. The value of $\overline{DP}_n$ is plotted vs. the dose in Figure 17 for the same experiment described by Figure 16. The invariance of $\overline{DP}_n$ is Figure 17 suggests that the decrease in G(-m) seen in Figure 16 for the same dose range is not caused by radiolysis of the oligomer because radiolysis of the oligomer should cause either an increase or decrease of $\overline{DP}_n$ depending upon whether crosslinking or fragmentation of the oligomer occurs more readily. The decrease in G(-m) is probably caused by interference of radiolysis products in the initiation and propagation steps of the polymerization, e.g., ethylene, which is found as a minor product, may inhibit initiation by capturing hydrogen atoms.

A high molecular weight fraction separated by gel permeation chromatography was shown by vapor pressure osmometry to have a $\overline{DP}_n = 7.0$. This suggests that the upper limit of the oligomer molecular weight is not much larger than 7 monomer units, i.e., no long chain polymers are obtained. The degree of polymerization may be affected by solutes which terminate polymer propagation by reacting with the growing polymer to produce a new radical which may or may not be able to initiate further polymerization. The concentration of such solutes produced via radiolytic decomposition of the monomer would increase with dose and therefore the value of $\overline{DP}_n$ should be dose dependent if the polymerization is dependent upon such termination. Some values of $\overline{DP}_n$ for a narrow range of dose

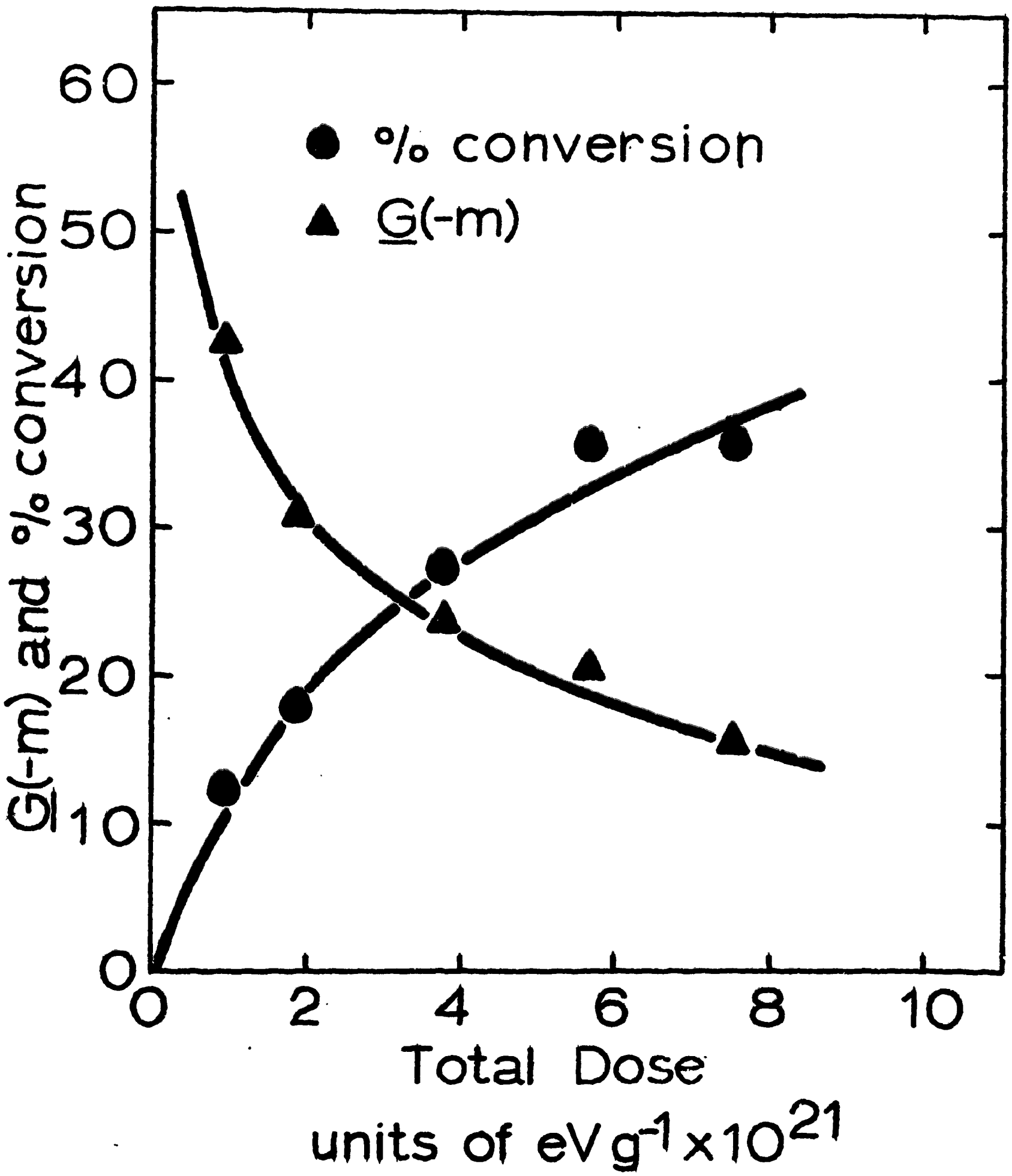



Figure 16. G(-m) and % conversion vs. total dose for 1-allyl-o-carborane at 31°.

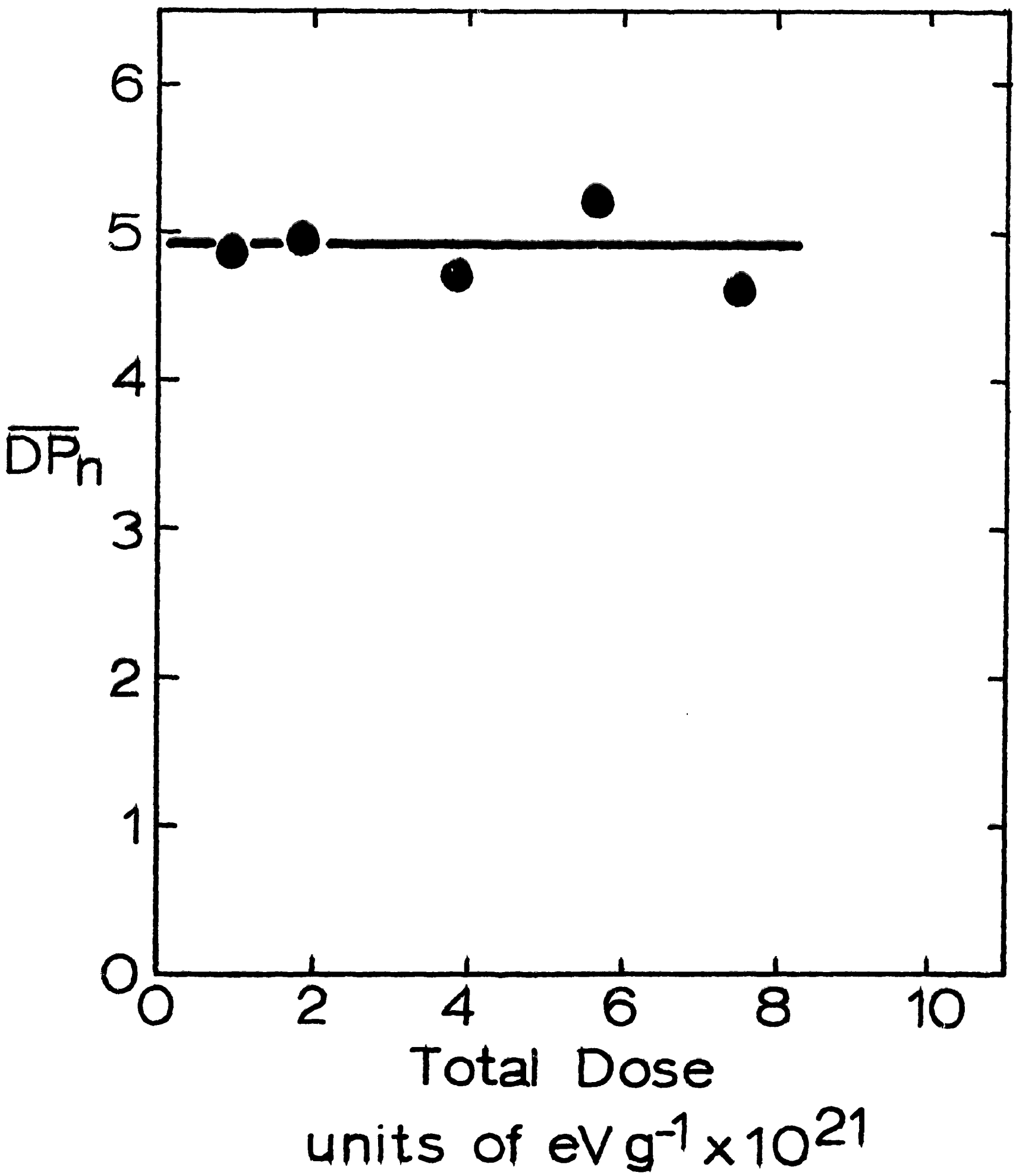



Figure 17. $\overline{DP}_n$ vs. total dose for 1-allyl-o-carborane at 31°.

rate, I, is shown in Table VI. The variation in these values is about the same magnitude as the experimental uncertainty in the points shown in Figure 17 and therefore nothing can be concluded yet about inhibition of degree of polymerization by radiolysis products.

The rate of polymerization, Rp, was obtained by weighing the amount of polymer separated from a known weight of irradiated monomer. A plot of $\log_{10}$ Rp *vs.* $\log_{10}$ I is shown in Figure 18. Simple polymerization kinetics predicts that Rp should be proportional to $I^n$ where the value of n depends upon mechanism of the polymerization. The slope of Figure 18 gives the value of n = 0.5 directly. Such a value suggests that the radiation-induced polymerization proceeds by a free-radical mechanism.[30] This value of n = 0.5 may be compared to a value of n = 0.76 obtained for radiolysis of VOC.[12]

Radiolysis of AOC also produced hydrogen, methane, ethane and ethylene. In contrast, no gases were found for irradiated VOC.[5] The yields of these gases are plotted *vs.* dose in Figures 19 and 20.

Structure analysis of oligomers-- The structure of the oligomer was examined to elucidate the reaction mechanism and to compare it with the structures assigned to oligomers of VOC.[5,6,13] The infrared and proton NMR spectra of the oligomer are recorded in Tables IV and V. Absorptions by the oligomer may be compared with those by the monomer. The infrared absorption at 6.12 μ by monomer is characteristic of an allyl double bond stretching frequency. The absence of this absorption band for the oligomer shows that the double bond has been eliminated in the oligomer. This suggests that the oligomer has a saturated backbone similar to a substituted polypropylene.

TABLE VI

Values of $\overline{DP}n$ for Several Dose Rates at 31°.*

| Dose rate $eV\ g^{-1}\ hr^{-1} \times 10^{19}$ | $\overline{DP}n$ |
|---|---|
| 2.22 | 5.05 |
| 2.56 | 4.37 |
| 2.86 | 3.44 |
| 3.91 | 4.69 |

* All samples were irradiated to a total dose of $3.8 \times 10^{21}$ $eV\ g^{-1}$.

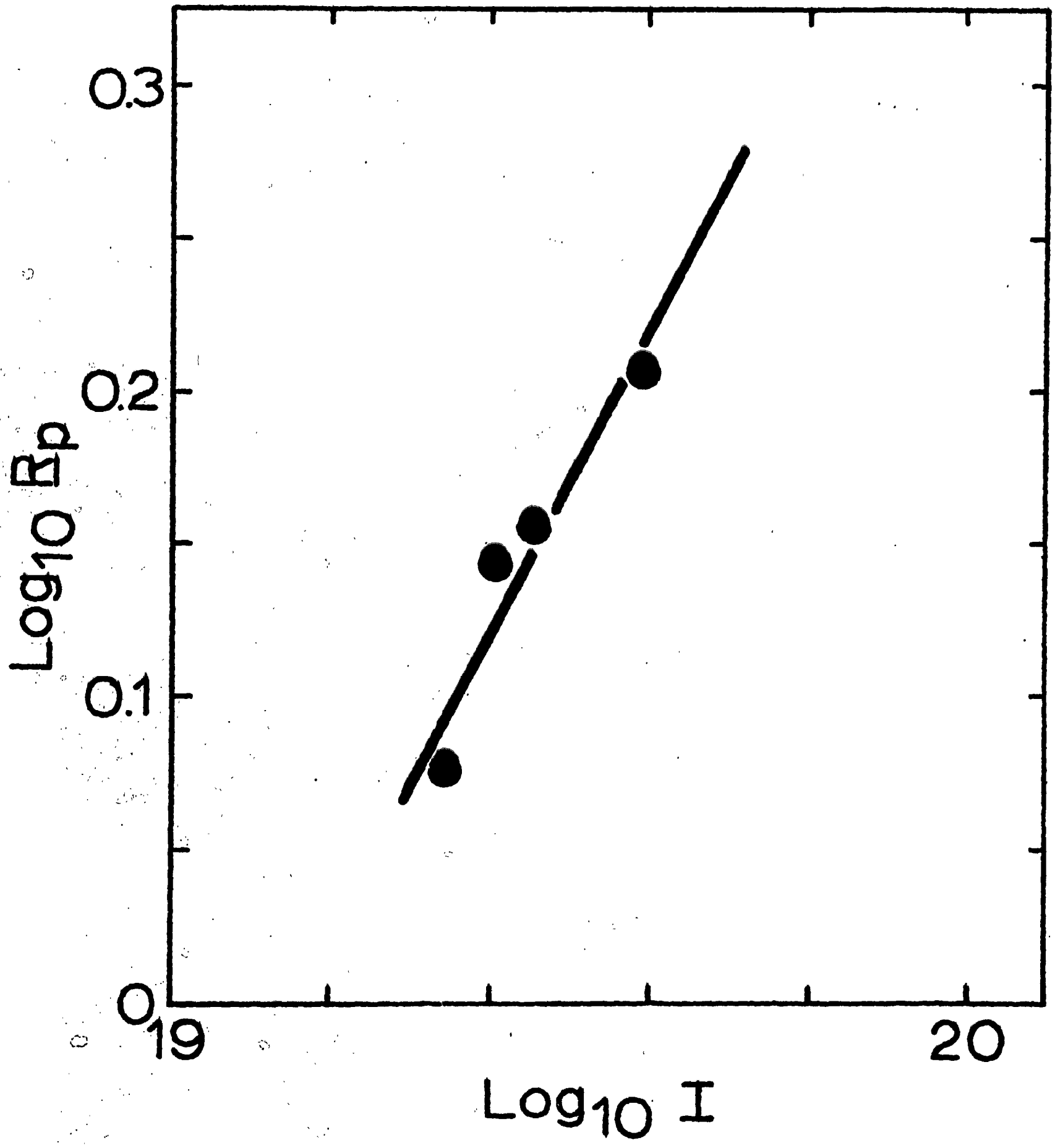



Figure 18. Rate of polymerization, Rp, vs. total dose for 1-allyl-o-carborane at 31°. I is in units of eV $g^{-1}$ $hr^{-1}$.

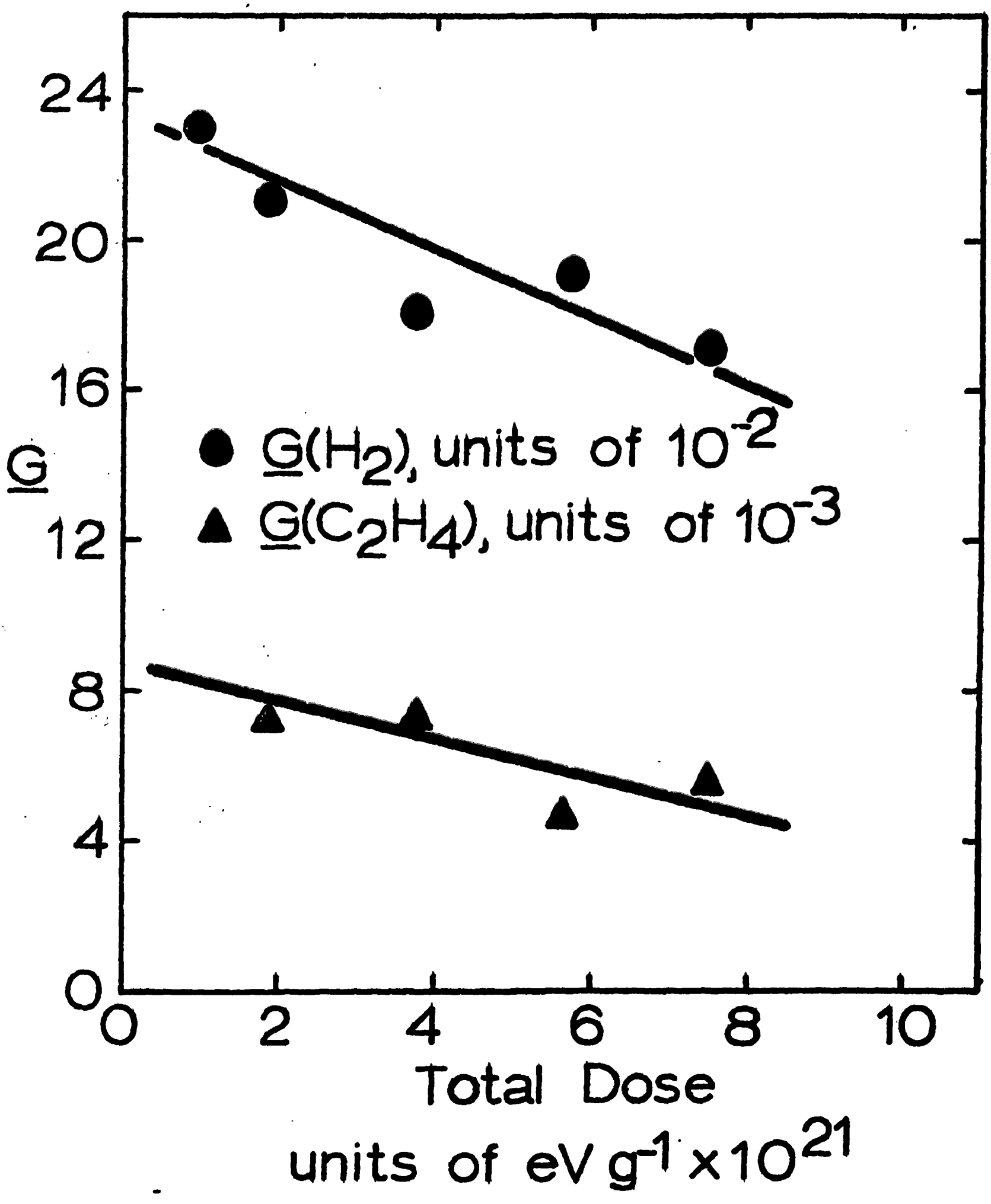



Figure 19. G(formation) for hydrogen and ethylene produced from 1-allyl-o-carborane irradiated at 31° with a dose rate of $3.91 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$.

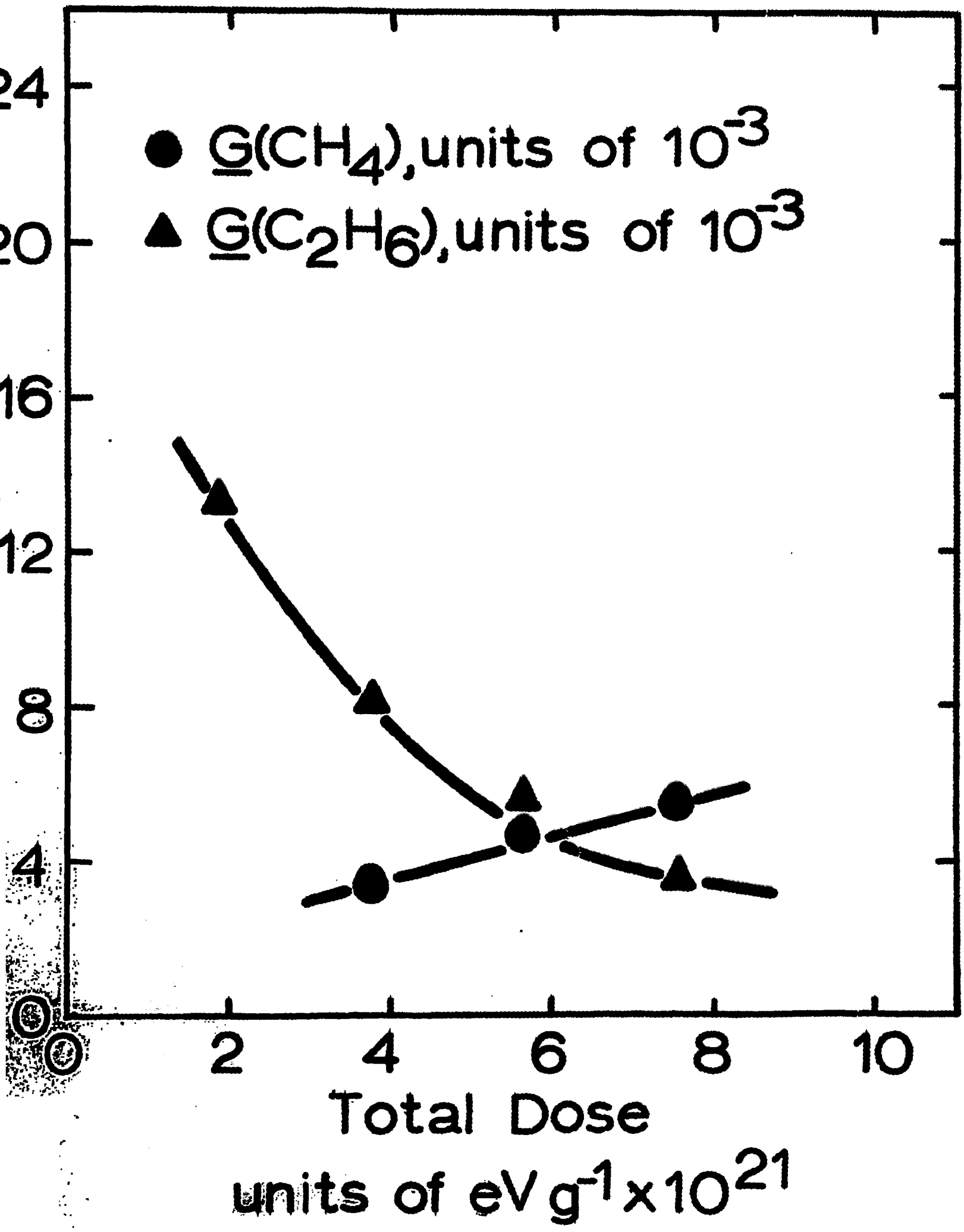



Figure 20. G(formation) for methane and ethane produced from 1-allyl-o-carborane irradiated at 31° with a dose rate of 3.91 x $10^{19}$ eV $g^{-1}$ $hr^{-1}$.

This would agree with the above indication of a free-radical mechanism for the oligomerization. The presence of the carborane cage in the oligomer is confirmed by the boron-hydrogen stretching absorption at 3.88 μ and by the cage absorption band centered at 14.00 μ. The proton NMR spectrum of AOC shows resonances at 2.90 and 5.42 ppm relative to TMS as standard which are assigned to the methylene and vinyl protons, respectively. The spectrum for the oligomer, as expected from the infrared evidence, does not show the vinyl protons, but two broad singlets appear upfield from the resonance at 3.52 ppm which is assigned to the proton bonded at C(2). These two singlets at 0.60 and 1.39 ppm are near methylene proton resonances found in polystyrene. Tentatively, these resonances are thus assigned to methylene protons in the carbon backbone of the oligomer. Better resolution of the NMR spectrum is anticipated by using more concentrated solutions of oligomer. Such solutions are expected by finding a better, more polar solvent for the oligomer than deuteriochloroform.

Radiolysis of AOC containing various solutes-- The addition of a low concentration of certain solutes to a monomer can change dramatically the course of radiation-initiated polymerization. In the present study, solutes shown in Table VII were added to pure AOC to give about 200 mM solutions. The yield of products from such solutions can be compared with that from pure AOC which was irradiated with the same dose rate of $3.9 \times 10^{18}$ eV $g^{-1}$ $hr^{-1}$ to the same dose of $3.8 \times 10^{21}$ eV $g^{-1}$.

Acetylene, not observed in radiolysis of pure AOC, is found as a product from all solutions. Oxygen is most efficient in

TABLE VII

Yields of Products from γ-Irradiated[1]
AOC Containing Various Solutes

| Solute[2] | G(-m) | G($H_2$) | G($CH_4$)[3] | G($C_2H_2$)[3] | G($C_2H_4$)[3] | G($C_2H_6$)[3] | DPn |
|---|---|---|---|---|---|---|---|
| none | 23.4 | 0.18 | 3.3 | 0 | 7.2 | 8.1 | 4.7 |
| $C_6H_{10}$ | 7.1 | 0.55 | 7.2 | 4.9 | 4.8 | 0.5 | 3.4 |
| $CH_3OH$ | 7.1 | 0.88 | 14.6 | 3.4 | 0 | 0 | 2.2 |
| $CHCl_3$ | 11.2 | 0.39 | 6.8 | 14.4 | 0 | 0 | 5.2 |
| $C_6H_6$ | 5.0 | 0.37 | 6.9 | 12.4 | 0 | 0 | |
| Pinene | 5.2 | 0.31 | 4.2 | 9.9 | 0 | 0 | 2.8 |
| $(C_2H_5)_2S$ | 5.0 | 0.23 | 4.5 | 2.1 | 2.7 | 1.3 | 5.2 |
| DPPH[4] | 10.0 | 0.39 | 4.5 | 9.0 | 0 | 0 | |
| $O_2$ | 11.1 | | 5.8 | 38.8 | 0 | 0 | |

1. All cells were irradiated with a dose rate of $3.9 \times 10^{19}$ eV $g^{-1}$ $hr^{-1}$ to a total dose of $3.8 \times 10^{21}$ eV $g^{-1}$.

2. Concentration of solute was 0.2 M.

3. Units of $10^{-3}$.

4. DPPH is 2,2-diphenyl-1-picrylhydrazyl.

promoting formation of acetylene. Ethylene and ethane are completely eliminated by solutes other than cyclohexene and diethyl sulfide. The latter solutes only reduce the yields of these two gases and as expected the yields of acetylene are less than those found for the other solutes except for methanol. For methanol, yields of methane and hydrogen are much higher than for the other solutes. The yield of hydrogen, the main gas product, is about doubled by all solutes except methanol and cyclohexene, and is nearly unchanged by diethyl sulfide. Although the explanation for all of these observations is yet unclear, the production of acetylene and the elimination of ethane and ethylene probably are not directly related to the reduction of $\underline{G}(-m)$. Polymerization and formation of hydrocarbon probably have different free-radical percursors. Because no hydrocarbon gases with more than two carbon atoms were detected as products, the precursor of ethane, ethylene and acetylene is probably an allylic radical which fragments between the carbons which are $\alpha$ and $\beta$ with respect to the carborane cage. The allylic radical has been observed by EPR in the irradiated solid at 77°K as discussed earlier in this report. The allylic radical is expected to be resonance stabilized[21] and therefore does not initiate polymerization. This is supported by the infrared and NMR spectra of the oligomers which showed that the oligomers have a saturated hydrocarbon backbone. Thus the allylic radical must react by coupling or unimolecular decomposition. Apparently decomposition leads to a radical, perhaps the ethenyl radical, which forms either ethylene or ethane or reacts with solute to form acetylene at the solute concentration used to obtain Table VII. Yields of polymer are coincidentally decreased probably owing

to reduction of the rate of initiation either by electron or hydrogen atom scavenging by the solute. The propyl radical, $\theta CH_2(CH_3)CH\cdot$, is probably the chain initiator. The polymer initiated by this free radical would be saturated as required by the infrared and NMR evidence. The yield of this propyl radical would be reduced by either hydrogen atom capture by solute or by prevention of hydrogen atom formation by solute, perhaps by electron capture or quenching of excited states of AOC which lead to hydrogen atoms. Hydrogen abstraction or disproportionation of the propyl radical is apparently not important because no 1-*n*-propyl-*o*-carborane was found as a product in this work.

A complete explanation of the radiolysis of AOC will be presented after work currently in progress can be used in the arguments, however it is now apparent that the radiation-initiated polymerization of pure AOC, unlike that of VOC, is complicated by some decomposition of the allyl substituent. The decrease of $G(-m)$ with increasing dose suggests that by-products of the radiolysis are interfering with the polymerization in a manner similar to the inhibition found for radiolysis of 1-isopropenyl-*o*-carborane, but not seen for VOC as discussed in ORO-3781-8.

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## CONTRACT PUBLICATIONS

### A. Publications

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

2. "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. R. Wright and T. J. Klingen, J. Inorg. and nucl. Chem., 32, 2853 (1970).

3. "Radiolytically Induced Polymer Formation in Alkenyl Carboranes: Phase Effects," T. J. Klingen and J. R. Wright, Mol. Cryst. Liq. Cryst., 13, 173 (1971).

4. "Further Evidence for the Plastic Crystalline Nature of 1-Vinyl-o-Carborane," T. J. Klingen and J. R. Wright, Mol. Cryst. Liq. Cryst., 16, 283 (1972).

5. "$^{1}$H-NMR Spectra of Icoshedral Carborane Polymers in Solution: Temperature Dependent Effects," J. R. Wright and T. J. Klingen, J. Inorg. nucl. Chem., 34, 3284 (1972).

6. "Investigation of Gamma-Ray Induced Polymer Formation in the Carboranes. II. Dynamics of the Polymerization of 1-Vinyl-o-Carborane in the Liquid and Plastic Crystalline States," J. R. Wright and T. J. Klingen, J. Inorg. nucl. Chem., 35, 53 (1973).

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8. "Charge Scavenging in the Gamma Radiolysis of Cyclohexane Solutions of Carboranes," R. M. Thibault, D. R. Hepburn, Jr., and T. J. Klingen, J. Phys. Chem., manuscript submitted for publication, October, 1973.

B. Patents

1. "Radiation Polymerization of Vinyl Carboranes and Novel Products Resulting Therefrom," T. J. Klingen and J. R. Wright, U. S. Patent Number 3,699,024, October 17, 1972.

2. "Optical Switching and Video Devices Using Organo-Substituted Carboranes," T. J. Klingen and J. R. Wright, U. S. Patent Number 3,711,180, January 16, 1973.

C. Meeting Papers, as yet not submitted for publication

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

2. "Free Radicals and Excited States of the Carboranes," T. J. Klingen and R. M. Thibault, 166th National American Chemical Society Meeting, Chicago, Ill., August, 1973.