Preparation of Alkali 9-Phenylfluorenide Solutions. For visible spectra, 0.050 mmol of 9-PhFlH in about 30 ml of THF was treated under reflux for 4 hr with excess potassium or for 12 hr with excess lithium or sodium. The orange solutions were filtered through sintered glass and diluted to 50.0 ml, giving 1.00×10^{-3} *M* solutions. Methanol was added to 10-ml aliquots with a 1-μl syringe. For ir and nmr spectra, 0.50 mmol of 9-PhFlH, 3 ml of THF, and alkali metal were stirred for 4 hr at ambient temperature, filtered, and diluted to 5.00 ml, giving 0.100 *M* solutions. Methanol was added to 1-ml aliquots with a 1-μl or a 50-μl syringe. Solutions of K^+9-PhFl$^-$ for nmr investigation turned black during preparation, probably because of formation of the dianion radical of 9-PhFlH.[25] The nmr spectrum of one such solution was broadened beyond recognition, but addition of a negligible amount of methanol (0.025 *M*) restored the carbanion color and its nmr spectrum. Solutions were transferred to standard quartz uv cells and covered with serum caps, to standard 0.1-mm sealed sodium chloride ir cells with Teflon plugs, and to standard nmr tubes with polyethylene caps and stored in sealed containers.

Visible Spectra. All spectra were recorded on a Cary-14 instrument in cells of 0.5–50 mm path lengths. With each solution the regions 250–450 nm and 450–560 nm were examined in two cells whose path lengths differed by a factor of 10. Some samples deteriorated rapidly, probably because of air leakage through or around the serum caps.[26] Oxidation could be detected by appearance of absorption maxima at 312 and 271 nm, which do not occur in either 9-PhFlH or 9-PhFl$^-$. Data were discarded unless absorbances of a solution could be reproduced to within 5% in spectra obtained 60 min apart, and no band or shoulder appeared at 312 or 271 nm. The spectra reported in Table I are average values of λ_{max} and ϵ from at least two independent preparations. Equilibrium constants for methanol protonation of 9-PhFl$^-$ (Table II) are averages of at least three determinations. Concentrations of M^+9-PhFl$^-$ were obtained from eq 3 using ratios of absorbance of the solutions containing methanol to absorbance of the corresponding solution containing no methanol at two to four different absorption maxima. Concentrations of other species in solution were calculated by eq 4–6, in which the subscript 0 refers to concentration

$$[\mathrm{M^+9\text{-}PhFl^-}] = \frac{\mathrm{abs}}{\mathrm{abs_0}} \times 10^{-3}\ M \qquad (3)$$

$$[\mathrm{9\text{-}PhFlH}] = 10^{-3}\ M - [\mathrm{M^+9\text{-}PhFl^-}] \qquad (4)$$

$$[\mathrm{MOCH_3}] = [\mathrm{M^+9\text{-}PhFl^-}]_0 - [\mathrm{M^+9\text{-}PhFl^-}] \qquad (5)$$

$$[\mathrm{CH_3OH}] = [\mathrm{CH_3OH}]_0 - [\mathrm{MOCH_3}] \qquad (6)$$

prior to addition of methanol or to the sum of concentrations of methanol and methoxide in solution.

Infrared Spectra. A Perkin-Elmer 521 instrument was used under normal qualitative conditions except that the chart abscissa was expanded twofold and absorption maxima were scanned at 70 cm^{-1}/min. Frequency was calibrated with the 3027.1-cm^{-1} band of polystyrene. The hydrogen-bonded ν_{OH} was so broad that the frequency measurements had an average deviation of ± 2 cm^{-1}.

Nmr Spectra. A Varian HA-100 instrument with a Varian V-4315 frequency counter was used in the field sweep mode. All proton chemical shifts in 9-PhFl$^-$ were determined relative to the α-methylene resonance of THF which was used as the lock signal. After completion of the 9-PhFl$^-$ spectra, tetramethylsilane was added to the sample and the chemical shift of the THF α-methylene resonance was determined relative to TMS. All reported chemical shifts are averages of 4–8 measurements. No spectral changes of solutions were found after samples had stood for 24 hr at ambient temperature. Concentrations of M^+9-PhFl$^-$ and 9-PhFlH in solution were determined from integrated areas >4.00 and <4.00 ppm from THF, which are ratios of 6:7 and 2:11 for M^+9-PhFl$^-$ and 9-PhFlH, respectively. Concentrations of CH_3OH and CH_3OM were determined by eq 5–6.

Acknowledgments. I thank the donors of the Petroleum Research Fund of the American Chemical Society for Grant No. 1351-G1 and the Esso Research and Engineering Company for a grant to the University of Illinois supporting this research.

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[25] (a) E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, **70**, 3021 (1966); (b) E. G. Janzen and J. G. Pacifici, *J. Amer. Chem. Soc.*, **87**, 5504 (1965).

[26] On a preparative scale a solution of K^+9-PhFl$^-$ in THF was autoxidized to an intermediate which gave 9-phenyl-9-fluorenol after neutralization in 79% crude yield as reported earlier by Sprinzak.[27]

[27] Y. Sprinzak, *J. Amer. Chem. Soc.*, **80**, 5449 (1958).

Radiation-Induced Reactions of 1,3-Cyclohexadiene

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Abstract: Irradiation of 1,3-cyclohexadiene with γ rays leads to dimerization either in solution or in the neat liquid. Relative amounts of the products vary widely with reaction conditions but the composition of the mixtures can be expressed as consisting of variable amounts of two groups. One set of products corresponds to those formed in thermal dimerization and the other has the distribution found in photodimerization mediated by triplet sensitizers. Formation of the "thermal" dimers is inhibited by isopropyl alcohol, a cation scavenger, and promoted by electron scavengers so a cationic mechanism is postulated. Ring cleavage to give 1,3,5-hexatriene is also observed and attributed to an excited singlet state of the diene. Since ring opening is not affected by electron scavengers we infer that excited singlets are formed in primary excitation processes and that triplets are produced by charge neutralization.

In a continuation of high-energy radiation chemistry studies of photochemically reactive compounds[1,2] we have investigated the γ radiolysis of 1,3-cyclohexadiene in organic solution.

Evidence based on a large number of experiments involving chemical reactions,[1,2,3–8] scintillation stud-

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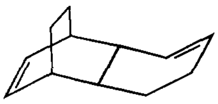
[1] R. A. Caldwell, D. G. Whitten, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 2659 (1966).

[2] G. S. Hammond, R. A. Caldwell, J. M. King, H. Kristinsson, and D. G. Whitten, *Photochem. Photobiol.*, 7, 695 (1968).

[3] R. R. Hentz, D. B. Peterson, S. B. Srivastava, H. F. Barzynski, and M. Burton, *J. Phys. Chem.*, **70**, 2362 (1966).

ies,[9-12] and pulse radiolysis[13-16] has demonstrated the formation of excited and ionized molecules in organic liquids under electron or γ radiolysis, and has also shown that transfer of molecular excitation energy or charge to other molecules can occur under energetically favorable conditions.

The compound 1,3-cyclohexadiene (CHD) appears to be well suited for the study of the nature and interrelations of the excited species formed during γ radiolysis. It undergoes a reaction which proceeds through the CHD triplet state to form the four dimers *endo*-dicyclohexadiene (**1**), *exo*-dicyclohexadiene (**3**), *trans,-cis,trans*-tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene (**2**), and the corresponding *cis,cis,cis* isomer (**4**).[17] Dimer **1** is only formed in trace amounts. Direct irradiation of liquid CHD yields 1,3,5-hexatriene,[18,19] believed to be produced from the singlet excited diene.[18] In addition to these photochemical reactions CHD also undergoes thermal dimerization in the liquid state at 200° to yield dimers **1** and **3**.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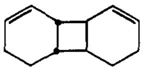
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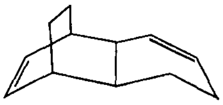
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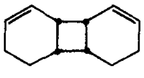
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The formation of dimers from CHD under the influence of ionizing radiation was first observed by Freeman and coworkers[20,21] who used the compound as a quencher in γ-irradiated aliphatic solutions. Another report[22] indicated that dimer **4** is formed by the radiolysis of CHD in benzene solution but that only polymer is produced in cyclohexane or in the neat liquid. The formation of a radiation-induced adduct between CHD and α-phellandrene (2-methyl-5-isopropyl-1,3-cyclohexadiene) has also been observed.[23] While our work was nearing completion we learned that a similar mechanistic study was also being completed by Schutte and Freeman.[24] Although there are minor discrepancies, the two investigations are in general agreement where there is overlap and in most respects conclusions concerning mechanisms are similar. Most of our experiments have been conducted in benzene solution or in neat CHD. Dimer yields were also measured in cyclohexane and pyridine without detailed investigation. Schutte and Freeman studied the reactions in benzene and several other solvents.

Experimental Section

Materials. Hinton zone-refined benzene (99.99%) was used as received. Aldrich 1,3-cyclohexadiene was distilled from lithium aluminum hydride under a nitrogen atmosphere, immediately degassed, and stored in sealed ampoules at <0°. Impurities were primarily cyclohexene (<4%), benzene (1–2%), and 1,4-cyclohexadiene (0.5%). Experiments involving analysis for C$_6$ products were carried out with CHD which had been purified by preparative gas chromatography on a $^3/_8$ in. × 6 ft β,β'-oxydipropionitrile column (cyclohexene, <0.4%; 1,4-cyclohexadiene, undetectable) prior to distillation and degassing. 2-Propanol (Matheson Coleman and Bell, spectroquality) and carbon tetrachloride (Baker, reagent) were used without further purification. *m*-Dinitrobenzene (Matheson Coleman and Bell) was recrystallized from benzene and sublimed.

Irradiation. Solutions of 1–3 ml were degassed and sealed in 13-mm diameter Pyrex ampoules, and irradiated in a ^{60}Co source. Standard Fricke dosimetry (G (Fe^{3+}) = 15.5) gave a dose rate of *ca.* 7 × 10^{19} eV/hr G H$_2$O, corrected for source decay and the electron densities of the solutions. Total doses were generally 10–11 × 10^{19} eV/cc. The temperature of the water-cooled irradiation cavity was approximately 30°.

A radiation source consisting of 100 mCi of Polonium-210 electrodeposited on a steel disk and sealed with a thin mica window was obtained from Nuclear Chicago Corporation. The irradiation cell was a disk-shaped glass container holding approximately 2 ml and with a thin aluminum window cemented over one face. The source and cell windows were kept 1 mm apart during radiolysis. The dose rate into the solution was approximately 10^{19} eV/hr, using G(Fe^{3+}) ≈ 5 for ^{210}Po α particles through a mica window.[25] The dosimeter solution was contained in an open cell with the surface approximately 1–2 mm away from the source window.

Analysis. Product analysis was by gas chromatography using flame ionization detectors. An internal standard was added after irradiation. Dimer composition was determined by using a 150 ft capillary (Golay) column coated with Apiezon L. All four dimers were separated by this column. Most of the yields of total dimer were measured on a $^1/_4$ in. × 8 ft column of 10% fluorosilicone (QF-1) coated on Diaport S support, using *n*-hexadecane (Matheson Coleman and Bell) as the internal standard. This column gave only partial separation of the dimers. Some analyses for total dimer were carried out with the capillary column, in which case *n*-dodecane (Matheson Coleman and Bell) was used as the internal standard. The two columns gave results which were identical within experimental error. The temperature of the gas chromatograph was maintained below 140° to prevent thermal isomerization of the dimers.

Samples of the dimers, both thermal and photolytic types, were prepared as previously described.[17] Their presence in the γ-irradiated solutions was confirmed by comparing retention times with those of the prepared dimers on the capillary and fluorosilicone columns as well as a β,β'-oxydipropionitrile column, the latter two giving only partial separation.

Authentic samples of *cis*- and *trans*-1,3,5-hexatriene were prepared by the method of Hwa, *et al.*[26] The *trans* isomer was obtained pure from the mixture by treatment with a small amount of I$_2$ followed by removal of the residual *cis*-triene by preparative vpc on the β,β'-oxydipropionitrile column used for CHD purification. The *cis* isomer was obtained pure by treatment of the mixture with

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(4) R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965).

(5) P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).

(6) G. Stein, "The Chemistry of Ionization and Excitation," Taylor and Francis, Ltd., London, 1967, p 25.

(7) M. Burton, "Second Tihany Symposium on Radiation Chemistry, Akademiai Kiado, Budapest, 1967, p 3.

(8) H. P. Lehman, *J. Phys. Chem.*, **73**, 20 (1969).

(9) J. A. Ward and W. H. Hamill, *J. Amer. Chem. Soc.*, **89**, 5116 (1967).

(10) R. R. Hentz and R. J. Knight, *J. Phys. Chem.*, **72**, 1783 (1968).

(11) P. K. Ludwig and M. M. Hugue, *J. Chem. Phys.*, **49**, 805 (1968).

(12) S. Lipsky and M. Burton, *ibid.*, **31**, 1221 (1959).

(13) R. Cooper and J. K. Thomas, *ibid.*, **48**, 5097 (1968).

(14) E. J. Land and A. J. Swallow, *Trans. Faraday Soc.*, **64**, 1247 (1968).

(15) F. S. Dainton, C. T. Peng, and G. A. Salmon, *J. Phys. Chem.*, **72**, 3801 (1968).

(16) T. J. Kemp, J. P. Roberts, G. A. Salmon, and G. F. Thompson, *ibid.*, **72**, 1464 (1968).

(17) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

(18) D. I. Schuster, F. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

(19) R. J. DeKoch, N. G. Minnaard, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **79**, 922 (1960).

(20) E. D. Stover and G. R. Freeman, *Can. J. Chem.* **46**, 2109 (1968).

(21) B. R. Wakeford and G. R. Freeman, *J. Phys. Chem.*, **68**, 2992 (1964).

(22) G. O. Schenck, S. P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **19B**, 19 (1964).

(23) C. H. Krauch, S. Farid, D. Hess, J. Kuhls, and W. Metzner, *Angew. Chem.*, **76**, 593 (1964).

(24) R. Schutte and G. R. Freeman, *J. Amer. Chem. Soc.*, **91**, 3715 (1969). We are indebted to Dr. Freeman for early communication of their results and for a preprint of the paper.

(25) J. Weiss and N. Miller, *J. Phys. Chem.*, **63**, 888 (1959).

(26) J. C. Hwa, P. L. DeBenneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **92**, 2537 (1960).

Table I

Solution	G(thermal)	G(photo)	G(**2**)/ G(photo)	[G(**3**) − 1/4.6G(**1**)]/ G(photo)	G(**4**)/ G(photo)
Neat CHD	2.04	3.12	0.57	0.22	0.21
1 *M* CHD in benzene	6.6	2.0	0.50	0.29	0.21
0.35 *M* CCl_4 in CHD	3.4	1.8	0.59	0.22	0.19
0.21 *M* CHD plus 0.33 *M* 2-propanol in benzene	0.29	0.92	0.57	0.24	0.19
Neat CHD, α radiolysis	Not known absolutely	1.5 × G(thermal)	0.59	0.20	0.21
0.21 *M* CHD in pyridine	0.05	0.51	0.57	0.22	0.21
0.21 *M* CHD in cyclohexane	4.8	0.7	0.48	0.32	0.20

maleic anhydride as described by Hwa. Infrared and ultraviolet absorption spectra were identical with those reported in the literature. The presence of these trienes in the γ-irradiated solutions was indicated by a comparison of retention times with authentic samples on β,β′-oxydipropionitrile and dimethylsulfolane columns. They were also isolated by preparative vpc from samples of pure CHD irradiated by a dose of 5×10^{21} eV/cc, allowing the uv spectra of both isomers formed in this way to be obtained. The nmr spectrum of the *trans* isomer was also obtained. These spectra agreed with the corresponding ones of authentic samples. Although it was not possible to isolate the *cis* isomer in sufficient concentration to obtain its nmr spectrum, the ultraviolet spectrum plus the fact that its conversion to the *trans* isomer, catalyzed by I_2, could be observed by vpc provides proof of its identity. Although 1,4-cyclohexadiene has the same vpc retention time as *cis*-1,3,5-hexatriene on both types of columns used, its uv spectrum and behavior in the presence of I_2 rule it out as the observed radiation product.

Results and Discussion

The γ radiolysis of CHD, both in benzene and in neat solution, yielded all four of the dimers previously observed photochemically and thermally. The photochemical studies have shown[27] that, for triplet-sensitized dimerization, dimers **2**, **3**, and **4** are formed with relative yields which are essentially independent of the sensitizer used. Using a large number of sensitizers, these relative yields have been found to be[28] 0.59 ± 0.03:0.23 ± 0.01:0.18 ± 0.02 for **2**:**3**:**4**. Unsensitized irradiation has been reported[22] to give a different distribution of dimers. However, we have found that at 2537 Å, the quantum yield for dimer formation in neat CHD, although finite, is less than 0.02, a value which is too small for this process to contribute appreciably to the observed yields at the radiation doses used. The relative yields of dimers **1** and **3** have been measured in a ratio of 4:1 when produced thermally.[17] We have remeasured this ratio by heating degassed CHD to 200° for 12 hr and have found the value 4.6:1 for **1**:**3**. Under γ radiolysis the relative yields of the four dimers vary widely with conditions such as concentration of CHD in solution or the presence of scavengers or sensitizers. However, it has been found that it is always true, within experimental error, that the dimer yields can be factored into two groups, one of which contains the dimers **1** and **3** in their thermal ratio. In the second group, dimers **2**, **3**, and **4** are found in the triplet-sensitized photochemical distribution. If 1/4.6 G(**1**) is subtracted from G(**3**), the remainder is the "photo" yield of **3**. Then if this factoring process is correct, G(**2**):G(**3**) − 1/4.6G(**1**):G(**4**) should exhibit the photochemical distribution of dimers, 0.59:0.23:0.18. That they do can be seen in Table I where representative examples of this factoring process for dimer yields measured under a variety of conditions are given. For the remainder of this paper, 5.6/4.6G(**1**) and G(**2**) + G(**3**) − 1/4.6G(**1**) + G(**4**) will be referred to as G(thermal) and G(photo), respectively.

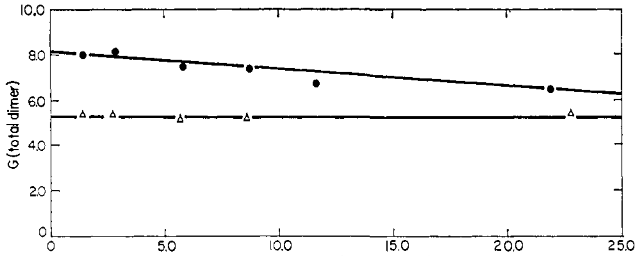

Figure 1. The dose dependence of G(dimer): ●, 0.21 *M* CHD in benzene; △, pure CHD.

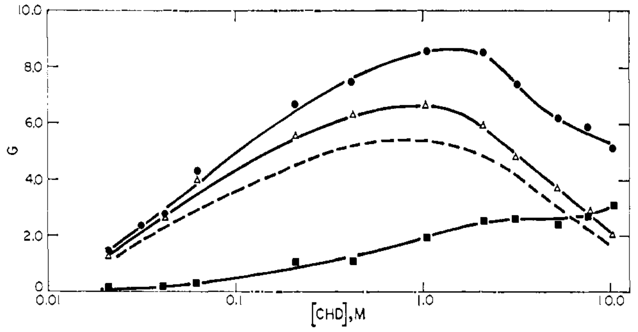

Figure 2. Yields of CHD dimers as a function of CHD concentration in benzene: ●, G(total dimer); △, G(thermal); ■, G-(photo); broken line, G(**1**).

Figure 1 illustrates the dose dependence of total dimer formation in pure diene and in 0.21 *M* CHD in benzene. The decrease in G with increasing dose in benzene solution was observed to be due to a dose dependence of G(photo), with G(thermal) remaining essentially constant.

Figure 2 gives the dependence of G(total dimer), G(thermal), and G(photo) on the concentration of CHD in benzene. The curve for G(thermal) has a maximum of 6.6 at approximately 1 *M*. The results are similar to, but not identical with, those observed in benzene by Schutte and Freeman.[24] The broken line in Figure 2 shows the variation in the yield of **1**, the only thermal dimer resolved by the analytical methods used by the

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(27) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 213.

(28) G. F. Vesely, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

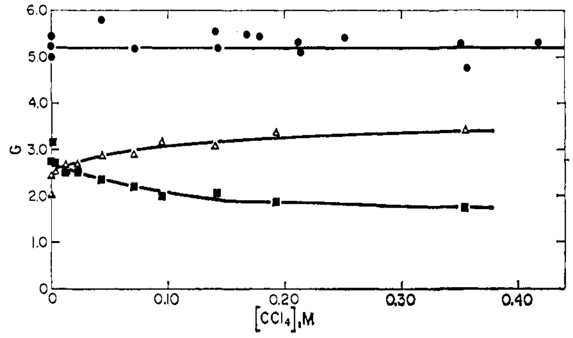

Figure 3. The effect of carbon tetrachloride on the dimer yield in neat CHD: ●, *G*(total dimer); △, *G*(thermal); ■, *G*(photo).

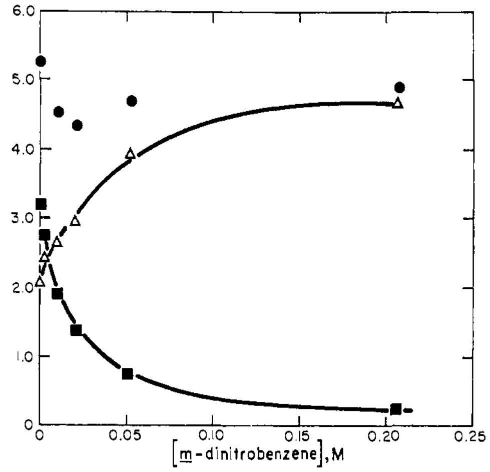

Figure 4. The effect of *m*-dinitrobenzene on the dimer yield in neat CHD: ●, *G*(total dimer); △, *G*(thermal); ■, *G*(photo).

latter workers. We find a maximum yield of this component of $G = 5.4$ at a diene concentration of 1.0 *M*. The Alberta group finds similar yields at that concentration but find a maximum of $G \cong 11$ at about 0.03 *M*, a concentration at which our yields were definitely falling. We do not understand the discrepancy but the agreement in results with higher diene concentrations is a good indication that the differences are due to subtle variations in reaction conditions rather than to trivial errors in analytical procedures. The fact that the temperature was higher in our experiments or that the solvents had different histories may be responsible Although all primary data reported in this paper were done using benzene purified by zone melting, we have observed that *G* values were about 20% higher when measurements were done using benzene purified by treatment with sulfuric acid. Curiously, our values are very close to those found by Freeman in methylcyclopentane[20] and cyclohexane solutions.[24]

The *G* values for thermal- and photodimers at low diene concentrations require solvent sensitization. On the basis of the *G* values in pure diene and the electron fraction of CHD in benzene, at 1 *M*, *G*(thermal) should be <0.2 and *G*(photo) should be <0.3 if there were no energy transfer from benzene.

The ability to partition the dimer yields into thermal and photo groups suggests that two processes occur, leading to these products. Various scavengers have been used to determine the precursors involved. Alcohols are used as cation quenchers.[29] The effect of 2-propanol on the dimer yield from 0.21 *M* CHD in benzene, given in Table II, is highly selective toward the thermal dimers.

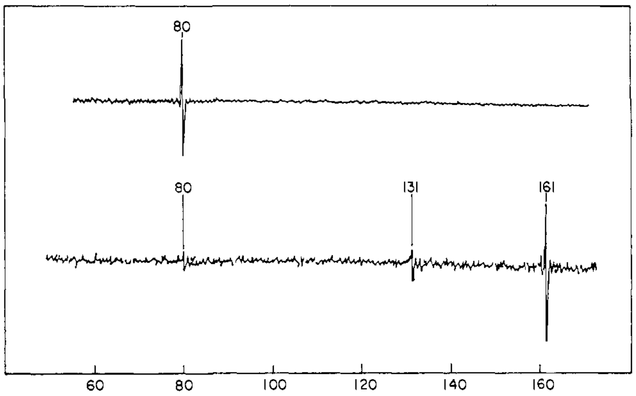

Figure 5. Ion cyclotron resonance spectra of CHD. Upper trace at 10^{-7} Torr and lower trace at 2×10^{-6} Torr.

Table II

2-Propanol (*M*)	*G*(thermal)	*G*(photo)
0	5.59	1.07
0.33	0.29	0.92
0.66	0.16	0.84

In neat CHD, the alcohol quenching effect is much reduced. Under these conditions no quenching is observed at a concentration of 0.1 *M* 2-propanol although at 1.2 *M* alcohol dimer formation is 53% quenched (based on energy into CHD only). This observation is consistent with a competition between CHD and 2-propanol for reaction with a CHD cation.

It was found that carbon tetrachloride, a commonly used electron scavenger, has a small effect on *G*(thermal) and *G*(photo) for 0.21 *M* CHD in benzene, enhancing the former and quenching the latter. The effect of this scavenger in neat CHD as shown in Figure 3 is qualitatively similar but more pronounced. *m*-Dinitrobenzene has also been used as an electron scavenger in neat CHD and the results are plotted in Figure 4. It has been demonstrated[30] that this compound is a good electron acceptor. It has also been found to be a strong electron scavenger in competitive scavenging studies with N_2O in ethanol.[31] Experiments showed that 0.6 *M* CCl_4 does not change the quantum yield of benzophenone-sensitized photodimerization in neat CHD. Thus this electron scavenger should not decrease the photo yield by direct triplet quenching. Both the cation and electron scavenger effects on *G*(thermal) argue in favor of a cationic precursor for the thermal dimers in benzene solution and in neat diene.

That the CHD radical cation can dimerize, at least in the gas phase, was demonstrated by experiments using the technique of ion cyclotron resonance (icr) spectroscopy.[32] The upper trace in Figure 5 shows the icr

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(29) J. W. Buchman and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

(30) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

(31) W. V. Sherman, *J. Phys. Chem.*, **70**, 2872 (1966).

(32) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

spectrum of CHD at 10 eV ionizing potential and 10^{-7} Torr CHD pressure. The parent ion is the only species present. The lower part of the figure shows that at the increased pressure of 2×10^{-6} Torr, the parent ion has almost all reacted, producing dimers and a small amount of fragmentation product. The 2 M + 1 mass number is probably due to stabilization of the "hot" dimeric ion by hydrogen abstraction from CHD. In condensed phase the excess energy resulting from dimer formation would be rapidly dissipated by nonchemical paths.

The effect of azulene, a good quencher of CHD triplets,[28] on the radiation-induced dimer yields was investigated. The addition of 0.002 *M* azulene to a solution of 0.21 *M* CHD in benzene quenches 84% of the photodimers and 52% of the thermal dimers.

Irradiation of a solution of 0.77 *M* benzophenone and 0.21 *M* CHD in benzene gave *G*(photo) = 2.4 (*vs.* 1.1 with no benzophenone) and essentially no thermal dimer. The effect of the triplet quencher, azulene, and the sensitizer, benzophenone, on *G*(photo) indicates a triplet precursor for these dimers. Both additives quench production of the thermal dimers. Since the ionization potential of benzophenone is lower than that of benzene (9.4 and 9.6 eV, respectively[33]) the effect here is probably due to scavenging of benzene cations, the precursor of the diene cations, by the benzophenone. The low concentration of azulene would prevent it from competing appreciably with CHD for benzene cations, but its ionization potential (7.4 eV[34]) is lower than that of CHD (8.4 eV[35]). It could therefore scavenge CHD cations as well as triplets, thus lowering *G*(thermal). The dimer factoring property also offers evidence in favor of a triplet mechanism since dimers **2**, **3** (corrected for the thermal contribution), and **4** appear in the ratio characteristic of the triplet sensitized reaction.

It is significant that in Figure 3, *G*(total dimer) remains unaffected by CCl_4; that is, in neat CHD the decrease in photodimers equals the increase in thermal dimers. This can be explained if the triplets that are quenched were formed by charge recombination. Inhibition of this neutralization by CCl_4 results in an increase in CHD cation concentration, and therefore of thermal dimers, equal to the decrease in triplet concentration.

The situation is somewhat more complex in the case of *m*-dinitrobenzene since, unlike CCl_4, it was observed to quench dimers in the benzophenone-sensitized photolysis of neat CHD. However, this quenching in the photochemical case is not accompanied by the formation of any thermal dimer. Thus in the radiation chemical case there are two mechanisms of triplet, and therefore photodimer, quenching. One is the result of electron scavenging and while it affects the dimer distribution it does not change *G*(total dimer). The other is a quenching of the CHD triplets which quenches photodimers. The extent of this second type of quenching is measured by the decrease in *G*(total dimer). Since the extent of triplet quenching is dependent on the concentration of triplets, it is also dependent on the extent of electron scavenging. This situation can lead to a minimum in the plot of *G*(total dimer) *vs. m*-dinitrobenzene concentration as observed in Figure 4. At high quencher concentrations most of the cations form thermal dimers rather than triplets and the triplet quenching is smaller than at intermediate concentrations where a greater fraction of the cations form diene triplets. The data of Figure 4, taken in conjunction with the quenching effect of *m*-dinitrobenzene in photosensitized dimerization, support the view that two quenching mechanisms are operative in the radiochemical system. At 0.04 *M m*-dinitrobenzene *G*(thermal) has increased by 1.6. This leaves a *G* of 1.6 of triplets available for photodimer formation. However, *G*(photo) is only 0.9 so that 44% of the triplets have been quenched. Within experimental error this is equal to the value of 52% obtained for the quenching of benzophenone-sensitized photodimerization at the same concentration of *m*-dinitrobenzene.

It can be seen from Figure 4 that at 0.2 *M m*-dinitrobenzene *G*(thermal) is 4.7 so that 81% of the photodimers formed in the absence of quencher have been converted to thermal dimers. This is therefore the minimum fraction of the cyclohexadiene triplets which are formed by charge recombination and direct triplet excitation accounts for a *G*(photo) of 0.6 or less. A similar charge recombination process has recently been proposed, on the basis of pulse radiolysis, as the sole mechanism for triplet production in irradiated benzene.[13] The constancy of the total yield of dimers in Figure 3 indicates that reaction 5 is the only significant fate of $(CHD)_2^+$ in pure CHD. If the dimeric ion reacted with CHD to form a trimeric ion, the yield of total dimers should be decreased by electron scavengers. On the other hand, if charge transfer to CHD were to occur leading to a chain mechanism for dimerization the total yield should be increased. We cannot rule out the possibility that both processes occur to about the same extent so that the effect of electron scavengers on both is fortuitously obscured. We will return to this subject later when discussing the reactions in benzene solution.

The dimerization mechanism in pure CHD can then be written

$$\mathrm{CHD} \rightsquigarrow \mathrm{CHD}^+ + e^- \tag{1}$$

$$\mathrm{CHD} \rightsquigarrow \mathrm{CHD}^3 \tag{2}$$

$$\mathrm{CHD}^+ + e^- \text{ (or } S^-) \longrightarrow \mathrm{CHD}^3 \tag{3}$$

$$\mathrm{CHD}^+ + \mathrm{CHD} \longrightarrow (\mathrm{CHD})_2^+ \tag{4}$$

$$(\mathrm{CHD})_2^+ + e^- \text{ (or } S^-) \longrightarrow \text{thermal dimers} \tag{5}$$

$$\mathrm{CHD}^3 + \mathrm{CHD} \longrightarrow \text{photo dimers} \tag{6}$$

$$e^- + S \longrightarrow S^- \tag{7}$$

The electron scavenging indicates that reaction 2 is a minor process. The formation of S^- inhibits reactions 3 and 5 by decreasing negative charge mobility.[36] This increases $[\mathrm{CHD}^+]$ at the expense of $[\mathrm{CHD}^3]$.

Scavenging of electrons by carbon tetrachloride is already 17% at 0.002 *M* scavenger, too low a concentration to scavenge effectively within spurs. Reaction 3 must involve, at least partially, electrons that escape from the original reaction sphere. In order to study this situation further CHD was irradiated with ^{210}Po α particles. The energy of these particles after passing through a mica window in the source and the 6×10^{-3} mm thick window of the sample cell was approximately 2 MeV, thus producing a much different spur geometry

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[33] A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Phys. Chem.* (Frankfurt am Main), **42**, 221 (1964).

[34] T. Kitagawa, H. Inokuchi, and K. Kodera, *J. Mol. Spectrosc.*, **21**, 267 (1966).

[35] A. D. Walsh, *Ann. Rep.*, **44**, 32 (1947).

[36] A. Hummel, *J. Chem. Phys.*, **49**, 4840 (1968).

than that produced by γ rays. The mean rate of linear energy transfer (LET) of the former is approximately 1000 times that of the latter.[37] The concentration of ion pairs in proximity should be enhanced by α-particle irradiation. If the concept of accelerated ion neutralization in spurs containing multiple ion pairs which has been suggested[38-40] is correct, neutralization in spurs to give triplets should result in an increase in the fraction of dimeric products appearing as photoproducts. In fact 54% of the dimers are now photo compared with 60% for γ irradiation. The lack of a LET effect indicates that the neutralization does not occur in spurs or that the proximity of more than one ion pair has no effect on their rate of neutralization.

Another interesting feature of the γ-induced reaction in pure diene is the production of a considerable amount of *cis*-1,3,5-hexatriene. This product is formed from the diene with a quantum yield of 0.46 ± 0.05, but none is produced in triplet-sensitized reactions. Therefore, we presume that the triene arises from excited singlet states of the diene. A G value of 1.58 was measured. The *trans* isomer was difficult to measure but was $<10\%$ of this value. Taken in conjunction with the photochemical quantum yield this indicates that the G value for production of excited singlet states may be as high as 3.4.[41] Within experimental error, *the yield of triene is not reduced by addition of carbon tetrachloride as a scavenger in concentrations up to 1 M. The difference between the effects of the electron scavenger on the yields of photo dimers and triene indicates that most of the excited singlets and triplets are not formed in parallel reactions.* Further evidence that charged species are not directly involved in singlet diene formation derives from the observation that 2-propanol in concentrations up to 1 M does not significantly affect the triene yield. We are not surprised that directly excited molecules, *i.e.* those not generated by ionization followed by charge neutralization, do not decay by way of the triplet manifold to an appreciable extent since this apparently does not occur to any significant extent in the photochemical experiments. We are rather puzzled by the indication that charge neutralization leads almost exclusively to formation of triplets. If the process were controlled by simple statistical factors alone, the ratio of triplet to singlet yields would be 3:1. Other factors must be important.

The reaction mechanism in benzene is obviously more complex than in pure diene because the solvent plays the role of sensitizer. Ionization and molecular excitation produced in the benzene can be transferred to the solute molecules. Creation of molecular excited states by charge neutralization can occur with cations derived from both the solvent and solute, although the insensitivity of G(photo) to 2-propanol at 0.21 M indicates that at least at this concentration most of the triplet diene is derived from triplet benzene. At the higher solute concentrations primary excitation must occur in both species to a significant extent. Finally, benzene may have a greater electron affinity than the diene[42] so electron mobilities may be decreased by the presence of benzene.

Schutte and Freeman[24] have pointed out that their maximum values for $G(\mathbf{1})$ are high enough to absolutely demand that some kind of chain process must be operative in the formation of thermal dimers. They suggest that reactions 8 and 9 occur to produce a chain mechanism.

$$(\mathrm{CHD})_2^+ \longrightarrow \mathrm{D}^+ \tag{8}$$

$$\mathrm{D}^+ + \mathrm{CHD} \longrightarrow \mathrm{D} + \mathrm{CHD}^+ \tag{9}$$

The falloff in yield at very high diene concentrations is then attributed to the incursion of reaction 10 which becomes competitive with cyclization of $(\mathrm{CHD})_2^+$ in reaction 8.

$$(\mathrm{CHD})_2^+ + \mathrm{CHD} \longrightarrow (\mathrm{CHD})_3^+ \tag{10}$$

Our results do not demand the chain mechanism on an energetic basis alone. The maximum yield of total dimers, observed in 1 M solution, was 8.6 molecules per 100 eV absorbed. Of this amount 6.6 was thermal dimer which must have come from ions and 2.0 was photo dimer, which has triplets as the immediate precursor. The ionization potential and triplet excitation energy[43] of benzene place a minimum of 70 eV required to produce the excitations. If the triplets also arise from ions, as we adduce to be the case in pure diene, the energy requirement would rise to 83 eV. This is considerably higher efficiency in utilization of absorbed energy for production of excited species than is usually indicated in such studies.[44,45] Such high efficiency in production of individual excited species would be surprising. We intuitively expect that some of the energy will be delivered in quanta large enough to promote molecules to levels well above the threshold for ionization so that a considerable fraction of the energy absorbed will be degraded directly to thermal modes. In summary, we are inclined to believe that a chain reaction, which is required to account for the results of the Alberta group, makes some contribution to the highest yields that we have measured.

As already stated, we believe that the chain mechanism disappears in neat diene and that reaction 10 is unimportant in the pure liquid. Consequently, we have reservations about the ingenious mechanism devised to account for the maximum in the yield of thermal dimers as the concentration of CHD is varied in benzene solution. A further indication of the inadequacy of the explanation can be gleaned from the quantitative discrepancy between the results obtained in the two laboratories. In both studies carefully purified materials were used so the differences must arise from the action of substances present in minute amounts. The rather close correspondence of results in pure CHD implies that the difference is due to foreign materials in some of the highly purified benzene. Since the offending substance or substances cannot be present in more than minute quantity the controlling role must be that of a scavenger. In principle the scavenger

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[37] W. G. Burns and R. Barker, *Progr. Reaction Kinetics*, **3**, 303 (1965).

[38] J. L. Magee, *Discussions Faraday Soc.*, **36**, 235 (1963).

[39] A. Mozumder and J. L. Magee, *J. Chem. Phys.*, **47**, 939 (1967).

[40] A. Hummel, A. O. Allen, and F. H. Watson, Jr., *ibid.*, **44**, 3431 (1966).

[41] Higher excited singlet states may be formed and suffer ring opening with efficiency greater than is observed photochemically. Consequently the estimate of G(singlet) is an upper limit.

[42] This, of course, means a smaller absolute numerical value since both electron affinities will be negative.

[43] G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963).

[44] W. P. Jesse, *ibid.*, **38**, 1187 (1963).

[45] G. G. Meisels, *ibid.*, **41**, 55 (1964).

could be either an electron trap present in Alberta benzene or a specific inhibitor of the chain reaction present in Pasadena benzene. Since the real interest in this work lies in understanding basic excitation mechanisms, elucidation of the details of the chain reaction is of secondary importance and we do not plan to pursue it further at this time. Once again we learn that caution must be exercised in using the *G* value for a radiation-induced reaction as a measure of the efficiency of a particular primary excitation mode.

The *G* value for production of 1,3,5-hexatriene was also measured in the experiments in benzene solution. *G* for *cis*-1,3-5-hexatriene production was 0.38 and that of the *trans* isomer was 0.09. Measurement of the *trans* yield was now possible since the CHD which interfered with the analysis in neat diene is now much reduced in concentration. This isomer now constitutes a much larger fraction of the triene than in pure CHD. Isomerization probably takes place through a triplet state of the *cis* isomer. Azulene quenches the isomerization almost completely although it does not quench the yield of *cis*. 2-Propanol has no effect on either isomer although 0.2 *M* carbon tetrachloride reduces both isomers by approximately 50%. Since the lowest benzene singlet has an energy level[46] which is probably below that of the lowest CHD singlet,[47] energy transfer to the diene may occur from a higher benzene singlet. Production of higher excited benzene singlets with a *G* of ∼1 which do not undergo internal conversion to the first excited singlet has been suggested from scintillator studies.[48] Energy transfer from such a state to anthracene has been proposed.[13] The quenching action of carbon tetrachloride may be due to hindrance of charge recombination to form benzene singlets. Alternatively it may quench the higher excited state of benzene directly. The lack of quenching action by 2-propanol indicates that benzene singlets are not formed from ions or that the alcohol is unable to quench benzene cations. This second possibility is consistent with the effect of 2-propanol in the quenching of dimers in benzene (Table II). Since *G*(photo) is negligibly affected beyond what is to be expected from radiation energy absorption by the alcohol, this too indicates the inability of 2-propanol to quench cations if the mechanism of Cooper and Thomas[13] for benzene triplet formation from ions is accepted.

Comparison with Thermal Dimerization. The fact that thermal reaction at 200° and the cationic process lead to the same dimeric products in the same ratio is striking. One might conclude that partitioning between paths leading to **1** and **3** occurs from a single high-energy intermediate formed in both processes. We do not at the moment have any easily believable candidates to suggest.

Conclusions. Two mechanisms, one involving triplets and one involving cation radicals, lead to formation of dimers of CHD under γ irradiation. In benzene solution the chain reaction suggested by Schutte and Freeman[24] can become important but is controlled by variables that we do not understand well.

Ring opening to 1,3,5-hexatriene is also observed and attributed to excited singlets of CHD. Excited singlets and triplets are apparently formed by independent mechanisms in neat cyclohexadiene. On the basis of electron scavenging experiments we conclude triplets are formed largely by charge neutralization. By a process of elimination, the same experiments indicate that higher singlets are produced in primary excitation processes.

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(46) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y., 1966, p 254.

(47) N. A. Allinger, J. Chow Tai, and T. N. Stuart, *Theor. Chim. Acta*, **8**, 101 (1967).

(48) P. Skarstad, R. Ma, and S. Lipsky, *Mol. Cryst.*, **4**, 3 (1968).