Radiation-Induced Dimerization of 1,3-Cyclohexadiene. Solvent Effects and the Formation of the Diels–Alder Dimers by a Cationic Chain Mechanism[1]

R. Schutte and G. R. Freeman

Contribution from the Chemistry Department, University of Alberta, Edmonton, Alberta, Canada. *Received October 30, 1968*

Abstract: The radiation-induced dimerization of 1,3-cyclohexadiene occurred by two simultaneous mechanisms: mechanism 1 produced mainly the *endo* and *exo* Diels–Alder products of 1,4,1′,2′ addition; mechanism 2 produced mainly the *cis–anti–cis* and *cis–syn–cis* isomeric products of 1,2,1′,2′ addition. Both mechanisms were sensitized by the aprotic solvents benzene, *n*-hexane, cyclohexane, and di-*n*-propyl ether, and were inhibited by the protic solvent ethanol. The relative efficiencies of the solvents for the sensitization of both mechanisms were: benzene > *n*-hexane ≈ cyclohexane > propyl ether. Mechanism 1 involved a cationic chain reaction in benzene, and probably also in the other aprotic solvents. In all the aprotic solvents the yield of the Diels–Alder products went through a maximum as the CHD concentration was increased. Thus mechanism 1 was inhibited by a large concentration of CHD. The maximum yield of the major Diels–Alder dimer I was larger if the maximum occurred at a lower CHD concentration. The values of $G(\mathrm{I})_{\max}$ and $[\mathrm{CHD}]_{\max}$ in each solvent were as follows: benzene, 11, 0.03 *M;* *n*-hexane, 6, 0.5 *M;* cyclohexane, 6, 0.7 *M;* di-*n*-propyl ether, 3, 4 *M*. There was no evidence of a chain in mechanism 2 and the yields of the corresponding dimers were relatively small. For example, in a 0.092 *M* solution of CHD in benzene, the *G* value of dimers from mechanism 1 was 16.3, while that from mechanism 2 was only 1.8. It appears that triplet-state CHD molecules were the immediate precursors of the dimers from mechanism 2, and that roughly half of the triplet CHD molecules resulted directly or indirectly from neutralization reactions.

Conjugated diolefins are efficient inhibitors in the radiolysis of several types of organic compounds.[2-5] When 1,3-cyclohexadiene (CHD) was added as inhibitor in the γ radiolysis of cyclohexene,[2] in addition to the expected inhibition reactions, dimerization of CHD occurred with a high yield; $G((\mathrm{CHD})_2)$ up to 6.3 was obtained. The structure of the dimer ruled out a free-radical mechanism for its formation. Charge scavenging alone could not account for the observed dimer yield, because *G*(total ionization) is about 4.2 for olefins in the gas phase[6] and is probably similar in the liquid phase. Charge scavenging in combination with energy transfer from excited molecules or energy transfer alone was proposed as being instrumental in the dimer formation.[2]

The dimerization of CHD occurs readily under a variety of circumstances.[7,8] However, the dimer is a mixture of isomers and the isomeric composition of the mixture is dependent on the method of preparation. Photosensitized dimerization yields mainly two isomeric products through a 1,2,1′,2′ addition reaction.[7,8] These isomers will henceforth be called 1,2 dimers. Heating of CHD gives dimers that are exclusively the *endo* and *exo* Diels–Alder products of 1,4,1′,2′ addition.[7-9] These isomers will henceforth be called 1,4 dimers. The photosensitized reaction also yields small amounts of the 1,4 dimers.[7,8] The behavior of CHD is in accordance with the theoretical considerations of Hoffmann and Woodward,[10] who stated that an electronically excited state of a conjugated diene adds preferably in the 1,2 mode to an olefin, and that the ground electronic state favors 1,4 addition (Diels–Alder reaction).

Elucidation of the mechanism of dimerization of CHD in solution during radiolysis thus seemed to provide a means of detecting electronically excited molecules through the formation of 1,2 dimers, and simultaneously detecting another type of excitation through the formation of 1,4 dimers. In the present work, three types of nonpolar solvent (aromatic, alicyclic, and aliphatic) and two types of polar solvent (protic and aprotic) were used.

Experimental Section

Materials. Benzene, cyclohexane, and *n*-hexane (Phillips Research Grade) were treated with concentrated sulfuric acid, washed with aqueous sodium bicarbonate and then several times with water, and dried with anhydrous magnesium sulfate. They were then distilled through a 60-cm Vigreux column, retaining the middle fraction. Finally, they were treated with a sodium metal mirror, degassed, and stored under vacuum.

Benzene-free absolute ethanol from Reliance Chemical Co. was used as received. Di-*n*-propyl ether (Eastman) was shaken with three batches of an equal quantity of aqueous ferrous sulfate, followed by three washings with an equal quantity of water. After a preliminary drying with magnesium sulfate, it was treated several times with sodium metal in a vacuum system. The final ether purity was 99.7%; none of the five measured impurities was an alcohol.

Sulfur hexafluoride and nitrous oxide (Matheson) were purified by trap-to-trap distillation, the first portion being pumped away. The minimum purities were 98.0 and 99.6%, respectively. Carbon tetrachloride (McArthur) and *n*-dodecane (Phillips) were used as received. Oxygen was purified by passing it over potassium hydroxide pellets and through a plug of phosphorus pentoxide; it was then condensed and given two trap-to-trap distillations, discarding the last 10% each time.

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[1] This work was supported in part by the Defence Research Board of Canada, Grant No. 1601-17.

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

[3] J. J. Myron and G. R. Freeman, *Can. J. Chem.*, **43**, 381 (1965).

[4] D. L. Dugle and G. R. Freeman, *Trans. Faraday Soc.*, **61**, 1166, 1174 (1965).

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

[6] G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

[7] G. O. Schenck, S. P. Mannsfeld, G. Schomburg, and C. H. Krauch, *Z. Naturforsch.*, **19B**, 18 (1964).

[8] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

[9] K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

[10] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

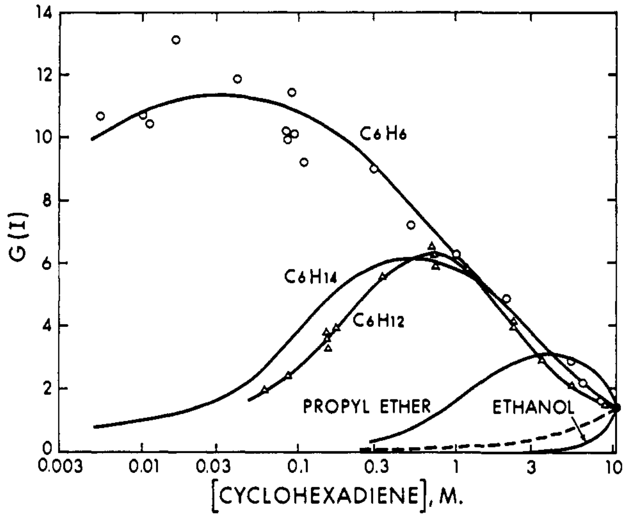


Figure 1. Yield of dimer I as a function of CHD concentration in different solvents. The dashed line approximately indicates the "expected" yield 1.4ϵ_c, where 1.4 is the yield of I in pure CHD and ϵ_c is the electron fraction of CHD in the solution. The curves through the benzene and cyclohexane results were calculated (see text). The curves for the other solvents were fitted empirically; the experimental points have been omitted for the sake of clarity.

1,3-Cyclohexadiene from Aldrich Chemical Co. usually contained <2% benzene, <5% cyclohexene, and <0.3% 1,4-cyclohexadiene. If necessary, the diene was purified by preparative glpc using β,β'-oxydiproprionitrile columns, so that the impurities never exceeded the above-mentioned limits. After drying with lithium aluminum hydride and distillation (bp 76.8–77.6° (700 Torr)), it was degassed and stored under vacuum in the dark.

1,4 dimers of CHD were prepared by heating 2.8 g of freshly distilled and degassed CHD for 15 hr in a sealed tube at 195°. The reaction mixture was then distilled and the dimers were redistilled: bp 80–86° (7 torr); yield 1.5 g.

1,2 dimers of CHD were prepared by a method previously described.[8] CHD (60 g) and 2-acetonaphthone (5.5 g) were dissolved in enough 2-methylbutane to give a total volume of 300 ml. Nitrogen was bubbled through the solution to remove oxygen. The solution was photolyzed for 22 hr by a Hanovia medium-pressure mercury lamp, surrounded by a water jacket, immersed in the solution. The reaction mixture was distilled and the dimer fraction was redistilled: bp 63–66° (2 Torr); yield 24 g.

Sample Preparation and Irradiation. The samples were prepared by standard vacuum techniques. The Ostwald absorption coefficient of nitrous oxide in cyclohexane was taken as 2.62,[11] and that of sulfur hexafluoride as 1.30.[12]

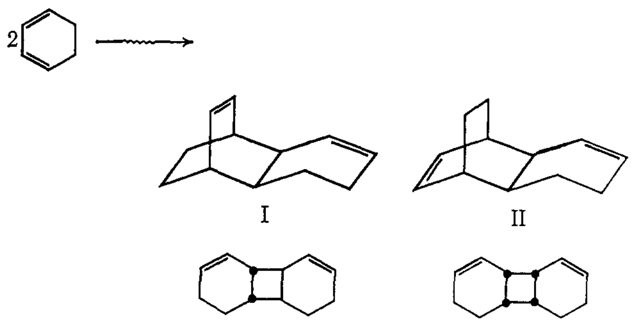
The γ-radiation absorbed dose rate was 4 × 10^{19} eV/(g hr), except when the effect of dose rate was being measured. The absorbed dose was $\leq 1.2 \times 10^{19}$ eV/g, such that conversion of the CHD did not exceed 13% even at the lowest initial CHD concentrations. The irradiation temperature was 23 ± 2°.

Analysis. After irradiation, the sample tube was opened and a measured amount of *n*-dodecane was added as an internal standard. An aliquot of the sample was then injected onto a 350 × 0.47 cm o.d. copper column packed with Diatoport WAW 60–80 mesh, coated with 2% w/w Silicone Rubber SE-30. Helium carrier and a hydrogen flame detector were used. To eliminate isomerization of the two heat-sensitive dimers of CHD (III and IV, see later), the temperatures of the injector and column did not exceed 150°. The detector was at 160°. The major 1,4 dimer (I) and the minor 1,2 dimer (IV) were well resolved and could be measured separately, but the minor 1,4 dimer (II) and the major 1,2 dimer (III) formed one peak and were measured together.

All four dimers of CHD were partially separated by a 4.5-m Apiezon L column, but the resolution was not sufficient to allow accurate measurement of any two of them separately.

Results

Products. Upon radiolysis of binary solutions of CHD in benzene, cyclohexane, *n*-hexane, di-*n*-propyl ether, or ethanol, the major C_{12} products were the four dimers of CHD, namely I to IV. Identification was made with the aid of several glpc columns and nmr, ir, and mass spectra. The spectra were consistent with the detailed structures proposed by earlier workers.[7,8]



When ethanol was the solvent, dimers I–IV were the major C_{12} products only in the more concentrated CHD solutions. In the dilute solutions the major C_{12} product was 2,2'-bicyclohexenyl.

Other C_{12} products identified were bicyclohexyl and cyclohexylcyclohexene in cyclohexane solutions and biphenyl in benzene solutions.

Effect of Dose. The yields of dimers of CHD in a benzene solution (0.098 *M* CHD) were measured as a function of dose over the range 1.25–18.0 × 10^{18} eV/g. The *G* values (the number of molecules formed per 100 eV absorbed) were calculated on the basis of the total energy absorbed by the sample: $G(\text{I}) = 8.6$, independent of dose; $G(\text{II} + \text{III})$ decreased from 4.6 to 3.9 with increasing dose; *G*(IV) decreased from 0.30 to 0.16. The yields in a cyclohexane solution (0.150 *M* CHD) were measured over the dose range 3.77–50.4 × 10^{18} eV/g: $G(\text{I}) = 3.35$, independent of dose; $G(\text{II} + \text{III})$ decreased from 1.62 to 1.38; *G*(IV) decreased from 0.09 to 0.04. The percentage variations over the 14-fold dose ranges were similar in the two solvents.

Since some of the product yields were sensitive to the magnitude of the dose used, most of the samples in the other experiments were given a constant dose of 1.2 × 10^{19} eV/g. However, to keep the CHD depletion to less than 15%, in the dilute solutions of CHD in benzene it was necessary to use lower doses.

Effect of Dose Rate. An increase of the dose rate over a 36-fold range (1–36 × 10^{18} eV/(g hr)) did not alter the dimer yields from a 0.098 *M* solution in benzene, and only about a 10% decrease occurred in a 0.144 *M* solution in cyclohexane.

Effect of CHD Concentration and of Solvent. The yield of the major 1,4 dimer I is plotted against CHD concentration in Figure 1. Five different solvents were used and there was a marked solvent effect. Four of the curves have maxima. The value of $G(\text{I})_{\text{max}}$ and the CHD concentration at the curve maximum for each solvent are as follows: benzene, 11 (0.03 *M*); *n*-hexane, 6.0 (0.5 *M*); cyclohexane, 6.3 (0.7 *M*); di-*n*-propyl ether, 3.1 (4 *M*). There was no maximum in the ethanol curve, and this curve fell below the others.

For CHD concentrations above 1 *M*, the curves for benzene, cyclohexane, and *n*-hexane almost coincide.

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[11] S. Sato, R. Yugeta, K. Shinsaka, and T. Terao, *Bull. Chem. Soc. Japan*, **39**, 156 (1966).

[12] S. Sato, T. Terao, M. Kono, and S. Shida, *ibid.*, **40**, 1818 (1967).

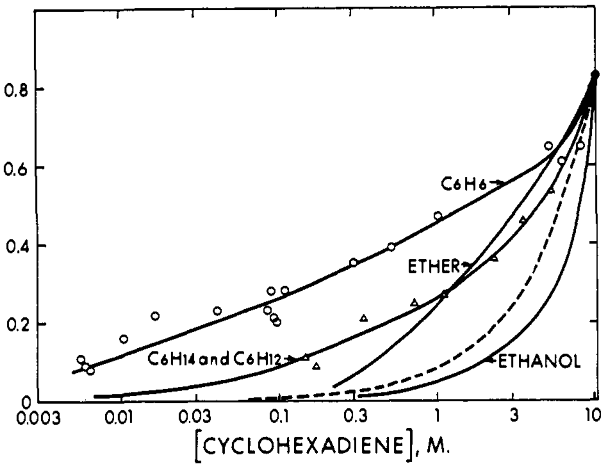

Figure 2. Yield of dimer IV as a function of CHD concentration in different solvents. The dashed line approximately indicates the "expected" yield $0.83\epsilon_c$, where 0.83 is *G*(IV) in pure CHD. The experimental points obtained with *n*-hexane, di-*n*-propyl ether, and ethanol solvents have been left off the curves, to prevent congestion.

The reproducibility of the results from the low concentrations of CHD in benzene was only about 15% from one batch of samples to another. Precision within one batch was ±5%. The reproducibility was much better in the other solvents. To show the magnitude of the scatter, the experimental points for the benzene and cyclohexane solutions are included in Figure 1. To avoid congestion of the figure, the experimental points for the other solvents have been omitted from the curves, but the amount of scatter was similar to that shown for cyclohexane.

The yield of the 1,2-dimer IV is plotted against CHD concentration in Figure 2. A continuous increase in *G*(IV) is observed with increasing CHD concentration in each of the solvents. The *n*-hexane and cyclohexane curves coincide.

The concentration dependence of the yield of I is quite different from that of the yield of IV.

The 1,4-dimer II and the 1,2-dimer III were not resolved by the gas chromatograph, so their combined yields show a complex concentration dependence that reflects a combination of Figures 1 and 2. In benzene solvent the yield of 1,4 dimers was large, so *G*(II + III) went through a maximum (Figure 3). In *n*-hexane and cyclohexane solvents *G*(II + III) exhibited a maximum and a minimum. There was not a maximum in the curve for either propyl ether or ethanol, because the yields of 1,4 dimers were relatively small in these solvents.

Effects of Scavengers. The addition of small amounts of ethanol to a benzene solution of CHD drastically reduced the yield of dimer I but had no effect on the yield of IV (Table I). The decrease in the yield of (II + III) presumably reflects the decrease in II, because the 1,2-dimer III should show the same behavior as IV.

Addition of ethanol to a cyclohexane solution of CHD decreased the yields of all the dimers (Table I). Addition of propyl ether to a cyclohexane solution decreased the yield of I but not of IV, similar to the effect of ethanol on the benzene solution.

Addition of the electron scavengers carbon tetrachloride, nitrous oxide, and sulfur hexafluoride increased the yield of I in cyclohexane solutions (Figures 4 and 5). The increase occurred for both low and high CHD concentrations, on both sides of the maximum in the *G*(I) curve displayed in Figure 1. By contrast, the electron scavengers lowered the yield of IV (Figures 4 and 5).

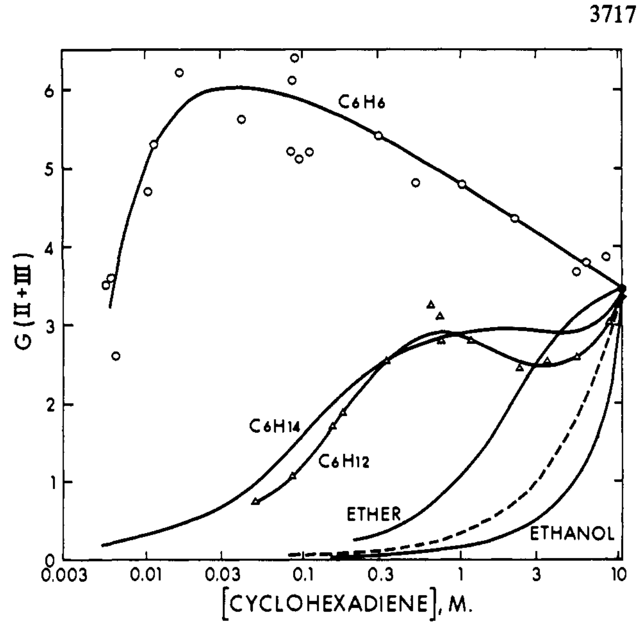

Figure 3. Yield of dimers II + III as a function of CHD concentration in different solvents. The dashed line approximately indicates the "expected" yield $3.4\epsilon_c$, where 3.4 is *G*(II + III) in pure CHD. The experimental points obtained with *n*-hexane, di-*n*-propyl ether, and ethanol solvents have been left off the curves, to prevent congestion.

Table I. Effect of Ethanol or Propyl Ether on the Yield of CHD Dimers in Benzene or Cyclohexane Solution

Solvent	[CHD], *M*	[Additive], *M*	*G*		
			I	II + III	IV
C_6H_6	0.092	None	11.4	6.36	0.28
		Ethanol			
		0.010	2.46	2.35	0.30
		0.041	0.60	1.70	0.30
		0.202	0.11	1.53	0.29
C_6H_{12}	0.161	None	3.78	1.71	0.10
		Ethanol			
		0.018	2.01	0.91	0.06
		0.068	0.65	0.29	0.03
		Propyl ether			
		0.010	2.44	1.33	0.11
		0.020	1.89	1.03	0.11
		0.040	1.39	0.92	0.11
		0.079	0.87	0.63	0.08

Carbon tetrachloride was added to three different CHD concentrations in benzene solvent; one (0.0055 *M*) was below, one (0.087 *M*) slightly above, and the other (5.5 *M*) much above the concentration at the maximum in the *G*(I) curve in Figure 1. The results are depicted in Figure 6. For the 0.0055 *M* CHD solution the yields of all the dimers are not affected by carbon tetrachloride, within experimental error. For the 0.087 *M* CHD solution *G*(I) remained constant while *G*(II + III) and *G*(IV) decreased slightly when carbon tetrachloride was added. In the 5.5 *M* CHD solution *G*(I) increased by 50% while *G*(II + III) and *G*(IV) decreased slightly.

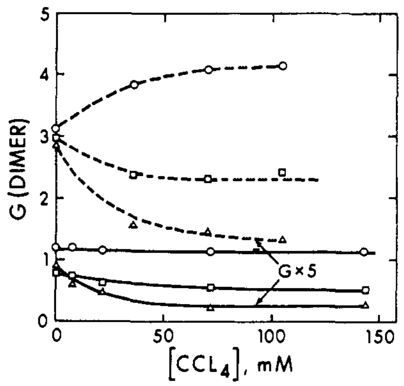

Figure 4. Effects of carbon tetrachloride on the dimer yields in cyclohexane solvent. ○, dimer I; □, dimers II + III; △, dimer IV. Full curves, 0.15 *M* CHD; dashed curves, 2.4 *M* CHD.

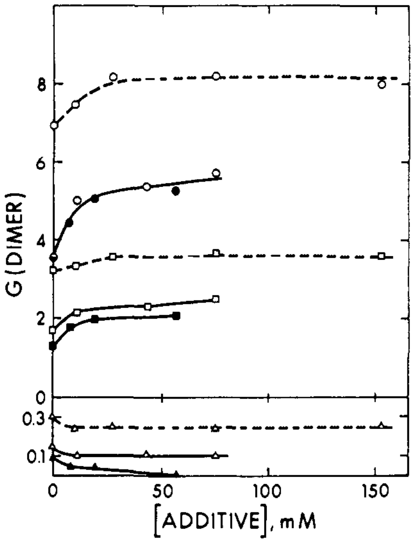

Figure 5. Effects of nitrous oxide and sulfur hexafluoride on the dimer yields in cyclohexane solvent: open points, nitrous oxide added; full points, sulfur hexafluoride added. Circles, dimer I; squares, dimers II + III; triangles, dimer IV. Full curves, 0.15 *M* CHD; dashed curves, 0.65 *M* CHD.

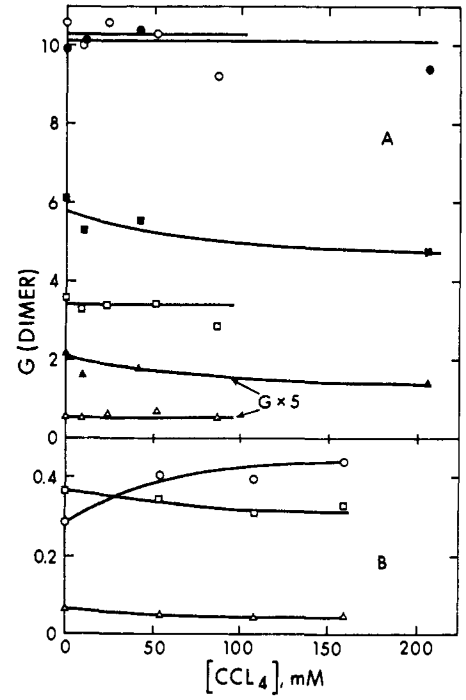

Figure 6. Effect of carbon tetrachloride on the dimer yields in benzene solvent. Circles, dimer I; squares, dimers II + III; triangles, dimer IV. A: open points, 0.0055 *M* CHD; full points, 0.087 *M* CHD. B: 5.4 *M* CHD.

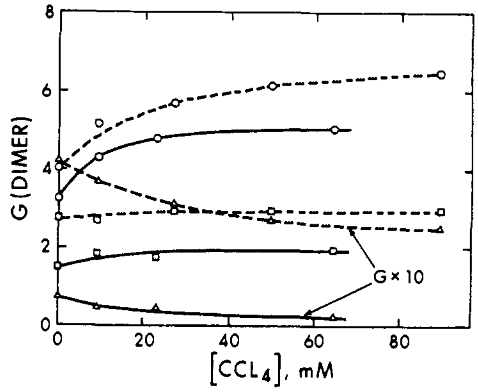

Figure 7. Effect of carbon tetrachloride on the dimer yields in di-*n*-propyl ether solvent. ○, dimer I; □, dimers II + III; △, dimer IV. Full curves, 0.75 *M* CHD; dashed curves, 4.2 *M* CHD.

Similar results were obtained with propyl ether solvent. At the lower CHD concentration (0.75 *M*) the addition of carbon tetrachloride caused no change in *G*(I), but decreased *G*(II + III) and *G*(IV), as shown in Figure 7. At the higher CHD concentration (4.2 *M*) the yield of I increased and those of (II + III) and IV decreased when carbon tetrachloride was added (Figure 7).

Oxygen was added to a cyclohexane solution of CHD of a concentration close to that where *G*(I) exhibited a maximum in Figure 1. Numerous new products were formed in addition to large amounts of polymer and the usual CHD dimers. At 0.05 *M* oxygen *G*(I) was increased by 0.8 unit, while *G*(II + III) was lowered by approximately the same amount. Dimer IV could not be measured in the oxygen containing solution, due to interference by new products.

Discussion

The aliphatic and alicyclic hydrocarbon solvents gave nearly the same results, but there were great differences between the results from each of the other solvents. The effects of the solvents and of the additives on the yields of dimers I and IV show that the two products are formed by different mechanisms. The behavior of the unresolved sum of the yields of II and III shows that both mechanisms contribute to the sum. Therefore, one can write

$$2\mathrm{CHD} \rightsquigarrow \mathrm{I, (II, III)} \tag{1}$$

$$2\mathrm{CHD} \rightsquigarrow \mathrm{IV, (II, III)} \tag{2}$$

In benzene solvent, reaction 1 was readily inhibited by ethanol, whereas reaction 2 was not. From the results in Table I one may deduce that for a 0.092 *M* solution of CHD in pure benzene, mechanism 1 gave $G(\mathrm{I})_1 = 11.4$ and $G(\mathrm{II} + \mathrm{III})_1 = 4.9$, while mechanism 2 gave $G(\mathrm{II} + \mathrm{III})_2 = 1.48$ and $G(\mathrm{IV})_2 = 0.29$. The ratio of the isomeric yields formed by mechanism 1 is therefore $[\mathrm{I}/(\mathrm{II} + \mathrm{III})_1] = 2.3$, and that from mechanism 2 is $[(\mathrm{II} + \mathrm{III})_2/\mathrm{IV}] = 5.1$.

Mechanisms 1 and 2 in the radiolysis system can be compared with the thermal and photolytic reactions, respectively. Heating CHD causes I and II to form.[7,8]

$$2\text{CHD} + \text{heat} \longrightarrow \text{I, II} \tag{3}$$

The ratio of the isomeric yields formed at 195° was I/II = 3.4 in the present work; values of the ratio reported earlier were 4 at 200°[8] and 3.2 at 220°.[7] The photolysis or photosensitization of CHD produces II, III, and IV.[7,8]

$$2\text{CHD} + h\nu \longrightarrow \text{II, III, IV} \tag{4}$$

Values of the ratio of the isomeric yields (II + III)/IV ranging from 2 to 19 have been obtained, depending on the reaction conditions.[7] The photosensitized reaction in the present work gave (II + III)/IV = 4.4, which compares with the value 4 reported earlier[8] for the same system.

At first it was tempting to identify mechanism 1 with 3, and 2 with 4. However, this has proved not to be true, because mechanisms 1 and 2 involve charged intermediates, whereas 3 and 4 do not.

Only dimers I and IV could be quantitatively measured separately, so the yields of I were used to devise details of mechanism 1, and the yields of IV were used to study mechanism 2.

Mechanism 1. The main, and perhaps exclusive, products of this mechanism are 1,4 dimers (Diels–Alder adducts).

The high yield of I in dilute benzene solutions, and to a lesser extent the yields in cyclohexane and *n*-hexane, strongly indicate that I is formed by a chain reaction in these solvents.

Addition of ethanol or propyl ether to the cyclohexane solutions sharply decreased *G*(I) (see Table I). Ethanol can scavenge positive ions in cyclohexane through proton abstraction from the hydrocarbon cations.[13] The proton affinity (PA) of ethanol is 193 ± 8 kcal/mole and that of the cyclohexyl radical is 174 ± 5 kcal/mole.[14] Extrapolation of the values of the PA for methanol, dimethyl ether, and ethanol[14] indicates that the PA of di-*n*-propyl ether is $\geq$200 kcal/mole. It therefore seems likely that ethanol and propyl ether inhibit mechanism 1 by scavenging positive ions.

Addition of oxygen to the cyclohexane–CHD system led to an increase in *G*(I). This virtually rules out a radical or excited molecule mechanism for the formation of I. Such mechanisms should have been inhibited or, at best, not affected by oxygen.

The electron scavengers nitrous oxide, sulfur hexafluoride, and carbon tetrachloride caused *G*(I) to increase. The increased yield caused by oxygen is also attributable to the effect of electron scavenging. These results are consistent with the suggestion that positive ions are involved in the dimerization. For example, the addition of an electron scavenger to solutions of cyclopropane in isopentane increased the radiolysis yield of *n*-propane, and this was attributed to increased lifetimes of the cations.[15] An increase in yield caused by the addition of electron scavengers does not necessarily indicate a cationic reaction, as illustrated by the negative ion chain isomerization of *cis*-2-butene that occurred when gaseous mixtures of *cis*-2-butene and sulfur hexafluoride were irradiated.[16] However, in the present case, the combined evidence of the positive ion and electron-scavenger effects leave only positive ions as possible precursors of dimer I.

G(I) decreases with increasing CHD concentration at the higher concentrations in benzene, cyclohexane, *n*-hexane, and propyl ether. This implies that CHD is itself an inhibitor of the reaction. The inhibiting reaction must be of a higher order with respect to CHD than is the rate-determining reaction in the formation of I at high CHD concentrations.

In summary, mechanism 1 should have the following properties: (a) dependent on the nature of the solvent; (b) inhibited by high concentrations of CHD; (c) inhibited by cation scavengers; (d) enhanced by electron scavengers. The following mechanism has these properties, although many of the kinetic details remain to be worked out. The reactions are written in terms of the formation of dimer I in solvent M, but it is understood that II and possibly some III are also formed by this mechanism

$$\text{M} \rightsquigarrow \text{M}^+ + \text{e}^- \tag{5}$$

$$\text{CHD} \rightsquigarrow \text{CHD}^+ + \text{e}^- \tag{6}$$

$$\text{M}^+ + \text{CHD} \longrightarrow \text{M} + \text{CHD}^+ \tag{7}$$

$$\text{CHD}^+ + \text{CHD} \longrightarrow \text{D}^+ \tag{8}$$

$$\text{D}^+ \longrightarrow \text{I}^+ \tag{9}$$

$$\text{CHD} + \text{D}^+ \longrightarrow \text{polymer}^+ \tag{10}$$

$$\text{I}^+ + \text{CHD} \longrightarrow \text{I} + \text{CHD}^+ \tag{11}$$

$$\text{e}^- + \text{S} \longrightarrow \text{S}^- \tag{12}$$

$$(\text{M}^+, \text{CHD}^+, \text{D}^+\ \text{I}^+) + (\text{e}^-, \text{S}^-) \longrightarrow \text{chain termination} \tag{13}$$

$$(\text{M}^+, \text{CHD}^+, \text{D}^+, \text{I}^+) + \text{Z} \longrightarrow \text{chain termination} \tag{14}$$

$$\text{polymer}^+ + (\text{e}^-, \text{S}^-) \longrightarrow \text{polymer} \tag{15}$$

where M+ is an ion capable of abstracting an electron from CHD, D+ is an intermediate that can rearrange to the positive ion of product I, S is an electron scavenger, and Z is any molecule that can react with a chain carrier to terminate the chain.

The propagation steps are (8), (9), and (11). The termination steps are (10), (13), and (14). The absence of a dose rate effect under the present reaction conditions indicates that (13) is negligible.

The dependence of *G*(I) on the nature of the solvent can be interpreted in terms of reactions 7 and 14. Concerning the former reaction, the yield of ions that are able to abstract an electron from CHD, and that live long enough to meet a CHD in the solution, may differ from one solvent to another. For example, in ethanol and in propyl ether reaction 7 rarely occurs because the M+ ions are rapidly removed by reaction 14, which in these cases are

$$\text{C}_2\text{H}_5\text{OH}^+ + \text{C}_2\text{H}_5\text{OH} \longrightarrow \text{C}_2\text{H}_5\text{OH}_2{}^+ + \text{C}_2\text{H}_5\text{O} \tag{14$'$}$$

$$(\text{C}_3\text{H}_7)_2\text{O}^+ + (\text{C}_3\text{H}_7)_2\text{O} \longrightarrow (\text{C}_3\text{H}_7)_2\text{OH}^+ + \text{C}_2\text{H}_5\text{CHOC}_3\text{H}_7 \tag{14$''$}$$

The $\text{C}_2\text{H}_5\text{OH}_2{}^+$ and $(\text{C}_3\text{H}_7)_2\text{OH}^+$ so produced do not abstract electrons from CHD. Furthermore, the small yields of I in ethanol solvent (Figure 1) indicate that ethanol also reacts with one or more of the ions CHD+, D+, and I+ (reaction 14).

The over-all neutral dimerization is estimated to be exothermic by 10–12 kcal/mole, and the ionization

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[13] J. W. Buchanan and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

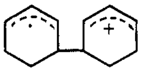
[14] G. R. Freeman, *Radiation Res. Rev.*, 1, 1 (1968).

[15] A. A. Scala, S. G. Lias, and P. Ausloos, *J. Am. Chem. Soc.*, **88**, 5701 (1966).

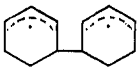
[16] R. W. Hummel, *Nature*, **218**, 1050 (1968).

potential of I is 10–12 kcal/mole greater than that of CHD.[17] Thus the over-all cationic dimerization is approximately thermoneutral.

The intermediate D^+ could have the structure V, by



V



VI

analogy with that (VI) suggested by Valentine and coworkers[8] to account for the isomerization of 1,2 dimers to 1,4 dimers at temperatures above 160°.

It can be shown, with the aid of simplifying assumptions,[18] that in the hydrocarbon solvents

$$G(\mathrm{I}) = \frac{aC}{C^2 + bC + d} \qquad \text{(i)}$$

where C is the concentration of CHD in mole/l.

For the solvent cyclohexane, the best fit of the experimental points was obtained with eq ii.

$$G(\mathrm{I}) = \frac{15C}{C^2 + 1.0C + 0.44} \qquad \text{(ii)}$$

Equation iii provided the best fit of the yields in benzene solvent.

$$G(\mathrm{I}) = \frac{12C}{C^2 + 1.0C + 0.001} \qquad \text{(iii)}$$

The curves for eq ii and iii are shown in Figure 1.

The initial slopes of the $G(\mathrm{I})$ *vs.* C curves in benzene and cyclohexane were finite (equal to a/d). By contrast, the initial slopes of these cruves were zero for propyl ether and ethanol solvents. This is because the rapid occurrence of reactions 14′ and 14″ in these solvents prevents (7) from taking place.

When reaction 7 does not occur, eq i is replaced by

$$G(\mathrm{I}) = \frac{aC\epsilon_c}{C^2 + b'C + d'} \qquad \text{(iv)}$$

where ϵ_c is the electron fraction of CHD in the solution and, under the conditions of the experiments, $b' \approx b$ and $d' \approx d$. The best fit with the propyl ether results for $C < 2$ mole/l. is obtained with eq v. At higher values

$$G(\mathrm{I}) = \frac{29C\epsilon_c}{C^2 + 0.04C + 0.84} \qquad \text{(v)}$$

of C, the experimental values of $G(\mathrm{I})$ fall above those calculated from eq v. Perhaps charge transfer from ether to CHD can occur when the two molecules are in contact at the instant that the ion is formed.

The values of the parameters in eq ii, iii, and v depend in complex ways on many factors, and no useful conclusions can yet be drawn from them.

The yields of I in ethanol solvent are so small that the approximations used in the derivation of eq i would not be valid. Equation i, therefore, does not apply to this solvent. The yields of I in ethanol even fell below those "expected" from the direct radiolysis of CHD: $G(\mathrm{I})_{\mathrm{expected}} = 1.4\epsilon_c$ (Figure 1). This implies that ethanol reacts with one or more of the ions CHD^+, D^+, and I^+ to prevent the formation of I.

Mechanism 2. The 1,2-dimer IV is a representative product of mechanism 2. Dimer III and possibly some of the 1,4-dimer II were also formed by this mechanism. However, both of mechanisms 1 and 2 contributed to the total yield of the poorly resolved pair of dimers II and III, so information about mechanism 2 was obtained from observations of the yield of IV.

The yields of IV from solutions of CHD in benzene, cyclohexane, hexane, and di-*n*-propyl ether were higher than those "expected" on the basis of the electron fraction of CHD in the solution (Figure 2). These solvents therefore sensitize the formation of IV. Conversely, ethanol inhibits the reaction (Figure 2). However, the yields are so small in all the solvents that it is improbable that the product is formed by a chain mechanism.

Triplet-state CHD is a possible precursor of IV.[8] Although CHD is also an efficient quencher of excited singlet states, the singlet quenching action apparently does not lead to the formation of CHD dimers.[19] According to the theory of Hoffmann and Woodward,[10] the 1,2 dimers could be formed from a CHD negative ion as well as from an electronically excited CHD molecule. However, a negative ion reaction would probably lead to a chain mechanism

$$\mathrm{CHD}^- + \mathrm{CHD} \longrightarrow \mathrm{IV}^- \qquad (16)$$

$$\mathrm{IV}^- + \mathrm{CHD} \longrightarrow \mathrm{IV} + \mathrm{CHD}^- \qquad (17)$$

which is analogous to that proposed for the *cis* → *trans* isomerization of *cis*-stilbene.[20] From what is known about electron affinities,[14] it seems likely that an electron could transfer from IV^- to CHD, because IV does not contain conjugated double bonds. A chain should therefore follow if reaction 16 occurs. There was no sign of a chain reaction with respect to the formation of 1,2 dimers, so reaction 16 is unlikely.

Electron scavengers lowered the yield of IV by 20–70% (Figures 4–7). Negative ions are therefore precursors to a fraction of the 1,2 dimers. The only alternative to reaction 16 seems to be that this portion of the 1,2 dimers is formed as a result of the neutralization reaction.

In summary, it appears that triplet-state CHD molecules are the immediate precursors of the 1,2 dimers, and that roughly half of the $^3\mathrm{CHD}$ molecules result directly

$$^3\mathrm{CHD} + \mathrm{CHD} \longrightarrow \mathrm{IV, III, (II?)} \qquad (18)$$

or indirectly from neutralization reactions.

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[17] R. Schutte, Ph.D. Thesis, University of Alberta, Edmonton, Alberta, Canada, 1968, pp 133–135.

[18] Reference 17, pp 137–145, 168–173.

[19] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3365 (1966).

[20] R. R. Hentz, K. Shima, and M. Burton, *J. Phys. Chem.*, 71, 461 (1967).