

Rate of Reaction of Hexahalocyclopentadienes with Long-Chain Olefins¹

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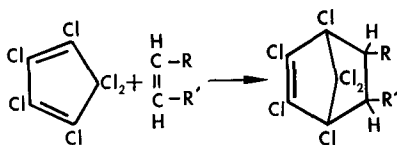
Abstract

Second-order rate constants were calculated for the Diels-Alder reaction of hexachlorocyclopentadiene and hexabromocyclopentadiene with various unsaturated fatty esters and a model alkene. Diene concentrations during reaction were determined by measurement of ultraviolet absorption at 322 m μ (hexachlorodiene) or 346 m μ (hexabromodiene). Steric factors in the specific perhalodiene used and, particularly, the structure of the olefins were shown to have pronounced effects on the rate of reaction of these highly substituted dienes.

Introduction

IN THE COURSE OF WORK on the preparation of flame-resistant urethane polymers from halogenated castor oil derivatives (4), including adducts of castor oil with hexachlorocyclopentadiene, it became necessary to determine optimum conditions for preparation of these adducts. Therefore the rates of reaction of hexachloro- and hexabromocyclopentadiene with castor oil and other long-chain olefins were determined. The effects of structural changes and temperature on these reaction rates were investigated.

As illustrated in Equation 1, the reaction of hexa-



chlorocyclopentadiene with olefins is a Diels-Alder type condensation. In the case of castor oil, reaction takes place at the 9,10-double bond of ricinoleic acid. Reactions of this type with fatty acid derivatives have been described by Fields (3) and others (1,6).

Materials

Materials used, as received from commercial suppliers, were castor oil (AA grade, Baker Castor Oil Company), hexachlorocyclopentadiene (C-56, Hooker Chemical Corporation or PCL, Velsicol Chemical Corp.), epoxidized soybean oil (Epoxygen, Type 90, General Mills Inc.), 1-octadecene and methyl elaidate (K & K Laboratories, Inc.), and methyl 10-undecenoate (Eastman Organic Chemicals).

Hexabromocyclopentadiene was prepared by reacting cyclopentadiene with potassium hypobromite (7). The product was a yellow crystalline compound melting at 86C.

Methyl oleate (>99% purity) was purified by chromatography in methanol solution on a silver-saturated ion exchange resin (2).

Methyl ricinoleate (>95% purity) was prepared by two successive distillations under reduced pressure

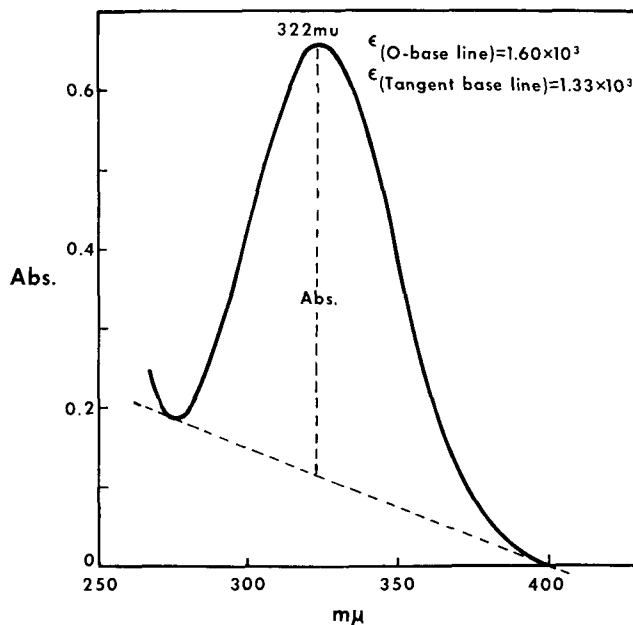


FIG. 1. UV absorption spectrum of hexachlorocyclopentadiene: 0.0374 moles/liter in tetrahydrofuran, 0.01099-cm cell path length.

of the mixed methyl esters which were obtained by alcoholysis of castor oil (8).

Methyl ricinoleate (>95% *trans*-isomer) was obtained by recrystallization of the product from isomerization of methyl ricinoleate (5).

Experimental Procedures

Measurement of Diene Concentrations

Diene concentrations were determined by measuring UV absorption of reaction mixtures. Hexachloro- and hexabromocyclopentadiene have absorption maxima at 322 and 347 m μ respectively, with extinction coefficients as indicated in Figures 1 and 2. Sample con-

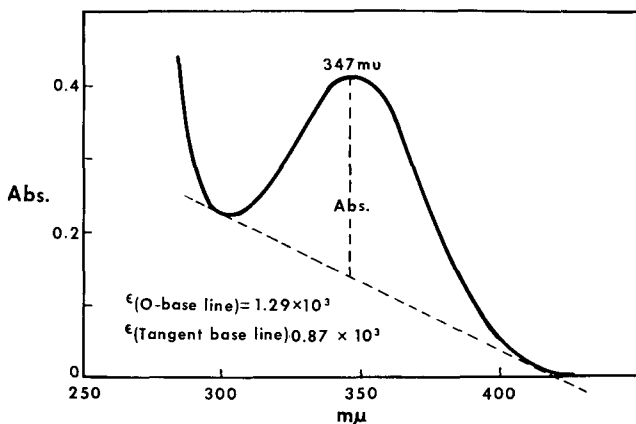


FIG. 2. UV absorption spectrum of hexabromocyclopentadiene: 0.0288 moles/liter in tetrahydrofuran, 0.01099-cm cell path length.

¹ Presented at the AOCs Meeting, New Orleans, May 1967 (Honorable mention, Bond Award Competition).

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centrations of about 0.2 g in 10 ml of tetrahydrofuran were used in a 0.01-cm quartz cell.

Mixtures of a diene with an olefin often darkened when heated and developed an increasing background UV absorption. To correct for this background absorption, a tangent base line was used as shown in Figures 1 and 2.

Determination of Reaction Rates

Fields (3) determined reaction rates by periodically measuring olefin concentrations by absorption of bromine at 0°C. In this work, reaction rates were calculated from diene concentrations, which were measured as described above.

Equimolar mixtures of diene and olefin were heated without solvent under nitrogen in small vials in a circulating air oven. Vials were removed at regular intervals and cooled prior to analysis of the contents. In some cases 10% epoxidized soybean oil was added as a stabilizer to reduce the development of dark colors and background UV absorption. The presence of this stabilizer had no significant effect on reaction-rate constants.

Rate constants were obtained from second-order rate plots as illustrated in Figure 3. These data are from the reaction of castor oil with hexachlorocyclopentadiene at 150°C. The diene concentrations at 0, 2, 4, 8, and 16 hr were 2.12, 1.71, 1.37, 1.02, and 0.65 moles/liter.

Results and Discussion

Temperature Effect and Activation Energy

To determine the effect of temperature on this reaction, castor oil was heated with hexachlorocyclopentadiene at temperatures between 110 and 180°C. The rate constants at 110, 130, 150, and 180°C were 1.7, 5.3, 18, and 83×10^{-6} liter/mole sec. By using the Arrhenius plot shown in Figure 4, the activation energy was calculated to be 19.5 kcal/mole. An activation energy of 20.3 kcal/mole has been reported (3) for the reaction of hexachlorocyclopentadiene with 4-methylcyclohexene.

Effect of Olefin Structure

Effect of olefin structure on the rate of reaction with hexachlorocyclopentadiene was investigated. Structural variations under study were location of the double bond in the aliphatic chain, presence of a

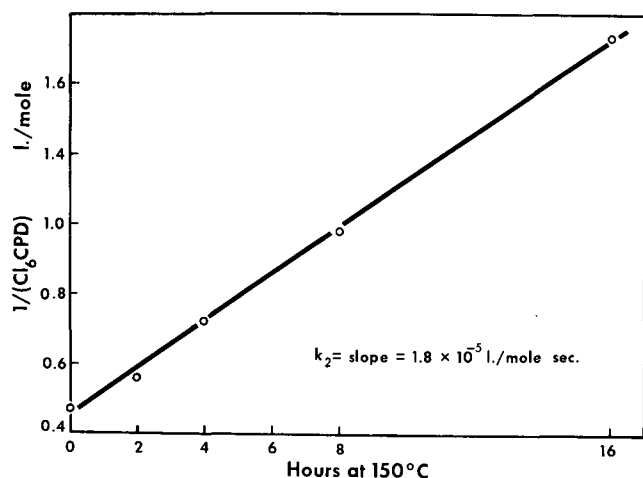


FIG. 3. Second-order rate plot for reaction of castor oil with hexachlorocyclopentadiene.

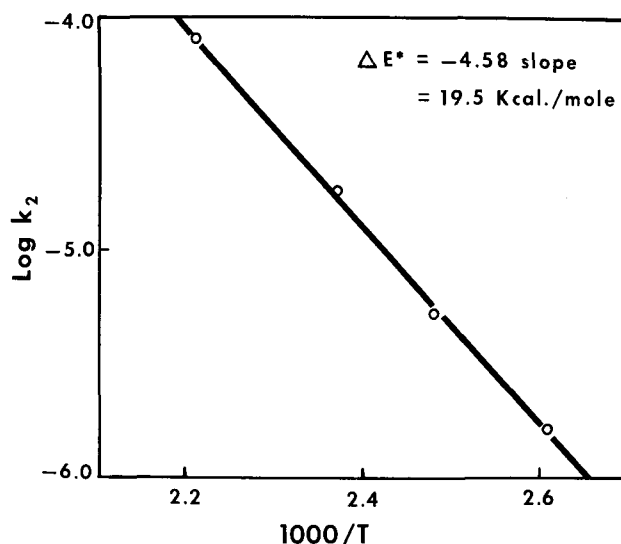


FIG. 4. Plot for calculation of activation energy from rate constants at different temperatures for reaction of castor oil with hexachlorocyclopentadiene.

homo-allylic hydroxyl group (e.g., ricinoleates), and the geometric configuration of the double bond.

The effect of bond location on reaction rates is indicated below:

Terminal	k_2 at 150°C liter/mole sec
1-octadecene	1.8×10^{-4}
methyl 10-undecenoate	2.4×10^{-4}
Mid-chain	
methyl oleate	2.8×10^{-5}

The terminal double bonds of 1-octadecene and methyl 10-undecenoate reacted 6–9 times faster with hexachlorocyclopentadiene than did the mid-chain double bond in methyl oleate. At 110°C the rate constant observed for 1-octadecene was 1.64×10^{-5} , which agrees well with 1.8×10^{-5} calculated by Fields (3) from the change in olefin concentration during this reaction.

The effect of the homo-allylic hydroxyl group in castor oil and other ricinoleates on the rate of this reaction may be seen in the rate constants listed below:

	k_2 at 150°C liter/mole sec
$-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-$ methyl oleate	2.8×10^{-5}
$-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{OH})-$ methyl ricinoleate	1.8×10^{-5}
castor oil	1.8×10^{-5}

Ricinoleic acid differs from oleic acid by having an hydroxyl group at carbon-12. The presence of this hydroxyl group reduced the reaction rate about 35%.

The rate constants listed below illustrate the effect of the geometric configuration of olefins on the reaction with hexachlorocyclopentadiene:

	k_2 at 150°C liter/mole sec
<i>cis</i>	
methyl oleate	2.8×10^{-5}
methyl ricinoleate	1.8×10^{-5}
<i>trans</i>	
methyl elaidate	4.9×10^{-6}
methyl ricinelaideate	3.8×10^{-6}

The *cis*-olefins reacted 5–6 times faster than the *trans*-olefins. Disappearance of the *trans*-double bond in methyl ricinelaideate during reaction was determined by measurement of the IR absorption at 10.3μ . The

rate constant at 150C, based on the concentrations of ricinelaide found, was 3.4×10^{-6} liter/mole sec. This agrees well with the rate calculated from concentrations of diene.

Effects of Diene Structure

Hexabromocyclopentadiene and its adducts are considerably less stable to heat than the corresponding chlorinated compounds. At 150C hexabromocyclopentadiene or mixtures of it with castor oil decomposed in 0.5–4 hr, even in the presence of 10% epoxidized soybean oil. However, at 130C, the epoxide-stabilized diene did not decompose in 7 hr. The reaction rates of hexabromo- and hexachlorocyclopentadiene were therefore compared at 130C. The second-order rate constants for reaction with castor oil are 3.5×10^{-6} for the hexabromodiene and 5.3×10^{-6} liter/mole sec for the hexachlorodiene.

These studies show that hexachlorocyclopentadiene adds more rapidly to long-chain olefins than does hexabromocyclopentadiene and that, in reactions with

hexachlorocyclopentadiene, terminal olefins react 6–9 times faster than mid-chain olefins, *beta*-hydroxy olefins react about two-thirds as fast as corresponding unsubstituted olefins, and *cis*-olefins react 5–6 times faster than *trans*-olefins. Steric factors thus appear to have a pronounced effect on the rate of reaction of these highly substituted dienes and should be considered when designing syntheses with these reactions.

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[Received August 25, 1967]