The Kinetics of Thermal Dimerization of Hexatriene

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Abstract

The thermal isomerization of *cis*-hexatriene (*c*HT) to cyclohexadiene (CHD) and the dimerization of CHD and *trans*-hexatriene (*t*HT) in the liquid phase in the temperature range 380 K–473 K are reported.

The rate coefficients are: for the *c*HT to CHD isomerization

$$\log k_2 = -(27{,}500 \pm 1500)/4.576\,T + (10.7 \pm 0.5)(\mathrm{s}^{-1})$$

for *t*HT dimerization

$$\log k_{3a} = -(23{,}100 \pm 300)/4.576\,T + (7.6 \pm 0.1)\ \ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

$$\log k_{3b} = -(22{,}400 \pm 1000)/4.576\,T + (7.6 \pm 0.1)\ \ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

$$\log k_{3c} = -(20{,}600 \pm 1500)/4.576\,T + (6.4 \pm 0.1)\ \ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

and for CHD dimerization; endo form

$$\log k_{5a} = -(23{,}200 \pm 1500)/4.576\,T + (6.1 \pm 0.2)\ \ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

exo form

$$\log k_{5b} = -(25{,}400 \pm 1500)/4.576\,T + (6.5 \pm 0.2)\ \ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$$

Introduction

In the process of studying laser enhanced bimolecular reactions in the gas phase, the formation and kinetics of thermally initiated dimerization of some C_6H_8 isomers was investigated since it was suspected to be a product channel of photoexcited, internally converted C_6H_8 isomers. In series of experiments we have followed the thermal and photo initiated isomerization, fission, and dimerization of 1,3-cyclohexadiene (CHD) and its isomers. Gas phase photoinitiated decomposition of CHD has two parallel channels, the formation of benzene and hydrogen and the formation of *cis*-hexatriene (*c*HT) which undergoes further isomerization to the *trans* form (*t*HT). In addition there are minor products. Some of the processes which are taking place are depicted in Scheme I.

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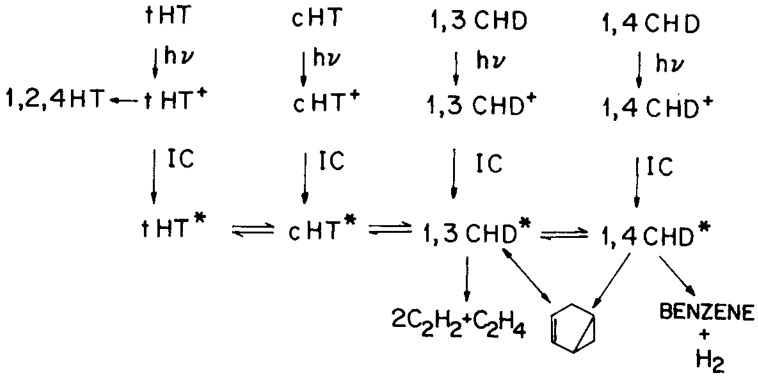
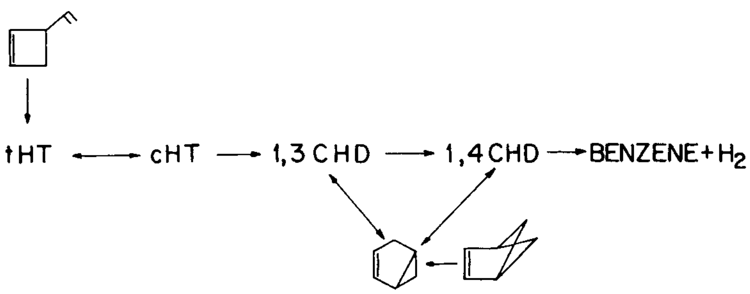


Scheme I

Elimination of H_2 is forbidden in the ground electronic state of 1,3-CHD but allowed from 1,4-CHD in a concerted reaction [1–4,6]. The internally converted 1,3-CHD undergoes isomerization via an intermediate to 1,4-CHD whenever the photon energy is in excess of the barrier hight of ca. 60 kcal/mol or to *c*HT which isomerizes further to *t*HT with activation energy of ca. 40 kcal/mol. Internal conversion takes place on a ns timescale [1–4] or faster [5]. Production of *c*HT is insensitive to pressure, indicating, an electronically excited molecule motions prior to a very fast internal conversion [5] of 8 ps.

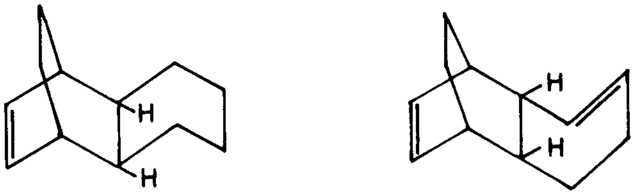
The thermal fission of 1,3-CHD [1,7,8] was studied and compared with that of 1,4-CHD [9–11]. The first reacts via a radical mechanism forming a radical +H atom which react to give products. 1,4-CHD reacts in a concerted reaction to give benzene and H_2.

Scheme II describes some of the thermal reactions which are taking place.



Scheme II

The dimerization of 1,3-CHD to exo and endo-dicyclohexadiene was studied in the gas and in the liquid states [12].



Structure I

It was found that the two products do not isomerize into each other in the gas or liquid state, therefore, it was suggested that they are formed in parallel reactions similar to dimers of cyclopentadiene [12]. The rate coefficients were found to be

$$\log k_{\text{exo}} = -25{,}100/4.576\,T + 5.97$$

$$\log k_{\text{endo}} = -24{,}300/4.576\,T + 6.08$$

in accord with the value obtained for similar Diels-Alder reactions. It is the purpose of the present work to study the dynamics of HT dimerizations as well as various intermediate steps in the thermal and photo reactions of some C_6H_8 isomers. Specifically, we have studied the following reactions:

(R1) $trans - 1,3,5 - \text{HT} \longrightarrow cis - 1,3,5 - \text{HT}$

(R2) $cis - 1,3,5 - \text{HT} \longrightarrow 1,3 - \text{CHD}$

(R3a) $2(trans - 1,3,5 - \text{HT}) \longrightarrow \text{dimer } a$

(R3b) $\longrightarrow \text{dimer } b$

(R3c) $\longrightarrow \text{dimer } c$

(R4) $2(cis - 1,3,5 - \text{HT}) \longrightarrow \text{dimer products}$

(R5a) $2(1,3 - \text{CHD}) \longrightarrow endo - \text{diCHD}$

(R5b) $\longrightarrow exo - \text{diCHD}$

The rate coefficients are denoted according to the reaction number, i.e., k_{3a} represents the rate coefficient of reaction 3a and so on.

Experimental

The chemicals used were 1,3-cyclohexadiene (Fluka, 97%), 1,3,5-hexatriene, mixture of *cis-trans*-isomers (ca. 2:3), (Aldrich, 97%), *n*-hexane (Riedel-deHaen 97%), and toluene (Merck 99,7%). Neat *cis*-1,3 hexatriene was obtained by treating the *cis,trans* mixture with maleic anhydride [13] until all the *trans* isomer was removed. This was followed by vacuum trap to trap distillation.

The reaction vessel was made from a stainless steel or a Pyrex cylinder i.d. 0.7 cm and length 4 cm. The reactor was heated by a temperature controlled oil-bath with heating time of less than 2 min.

All experiments were done in liquid toluene or *n*-hexane. The concentrations used are [CHD] = 0.1 M − 0.5 M; [*t*HT] = 3 10^{-2} M − 0.25 M; [*c*HT] = 2 10^{-2} M − 0.15 M. All kinetic data are independent of solvents.

All the kinetic data were analyzed by vapor-phase chromatography with a megabor-type column (0.53 mm i.d., 30 m length), HP-1 phase (0.88 μm thickness) with He as a carrier gas (5.8 ml/min, split 1/10) and a FID detector. The identification of the products was done by GC-MS (Finnigan ITS 40), column DB-5 (30 m × 0.25 mm), 0.25 μm film thickness and by ^{13}C-NMR (Bruker 400AC). Peaks were calibrated by a calibration curve.

Results and Discussion

*c*HT undergoes fast isomerization to CHD, much faster than it dimerizes. Therefore, the decay of *c*HT obeys a first-order decay, as can be seen from Figure 1 where the logarithm of the concentration of *c*HT is given as a function of time at 380 K. In contrast, the rate of isomerization of *t*HT to *c*HT is slow compared with the rate of dimerization. Therefore, a second-order kinetics is expected and is observed as can be seen from Figure 2 where the inverse of the concentration of *t*HT at 380 K is plotted vs. time (see Appendix). Such a linear graph is what is expected from a second-order kinetics. Three dimers were observed to form during the reaction. Second-order plots of the inverse of the concentration of the dimer vs. the inverse of the time yield straight lines as expected. Figure 3 show sample results for the three dimers.

To make sure that the *c*HT → CHD is the prominent process, we have compared the rate of disappearance of *c*HT and the rate of appearance of CHD. The rate coefficients of the two processes are given in the Arrhenius plot, Figure 4. As can be seen the rates of appearance and disappearance are equal over the temperature range studied. The rate coefficient for *c*HT isomerization is

$$\log k_2 = -(27{,}500 \pm 1500)/4.576\,T + (10.7 \pm 0.5)(\mathrm{s}^{-1})$$

This value is similar to one obtained previously [14].

The dependence of the rate coefficient for the disappearance of *t*HT and the rate coefficient for the appearance of the dimers is given in Figure 5.

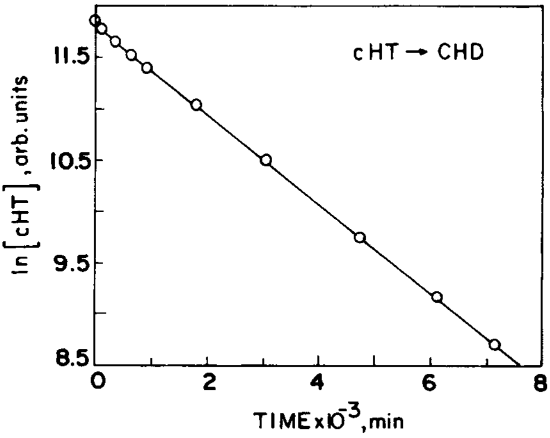


Figure 1. Logarithm of the concentration of *cis*-hexatriene (arbitrary units) vs. time at 380 K.

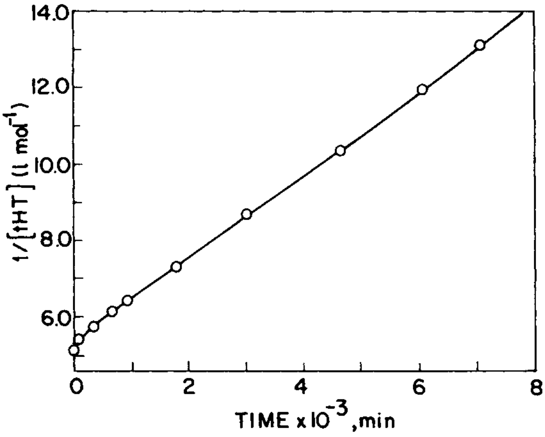


Figure 2. Inverse of *trans*-hexatriene (ℓ mol^{-1}) vs. time. Dimerizations at 380 K.

The rate coefficient for the disappearance of *t*HT is given by

$$\log k = -(22{,}150 \pm 1000)/4.576\, T + (7.85 \pm 0.1)(\ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$$

The rate of disappearance of HT is twice the rate of appearance of the dimers and $k = k_{3a} + k_{3b} + k_{3c}$ (see appendix for details). The rate coeffi-

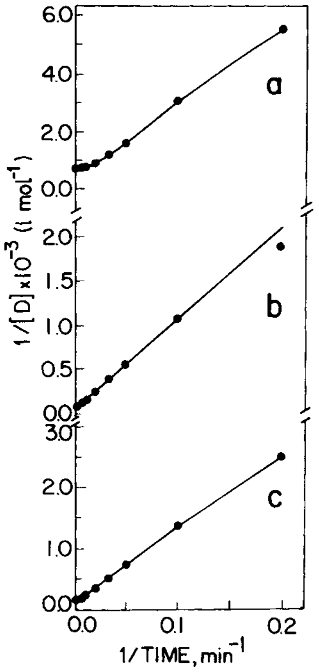


Figure 3. Inverse of dimers concentrations (ℓ mol^{-1}) vs. inverse time. a, b, and c are the three dimers formed from *t*HT at 423 K.

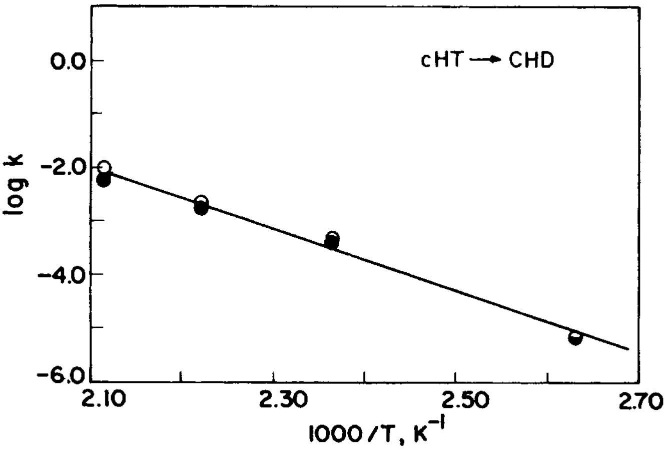


Figure 4. Log *k* vs. inverse temperature for the decay of *c*HT (○) and the formation of CHD (●).

cients for the appearance of the three dimers are

$$\log k_{3a} = -(23{,}100 \pm 300)/4.576\,T + (7.6 + 0.1)(\ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$$

$$\log k_{3b} = -(22{,}400 \pm 1000)/4.576\,T + (7.6 \pm 0.1)(\ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$$

$$\log k_{3c} = -(20{,}600 \pm 1500)/4.576\,T + (6.4 \pm 0.1)(\ell\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1})$$

The sum of the inverse of the intercepts of the 3 graphs of the inverse of dimer concentration vs. time should be $[t\mathrm{HT}]_0/2$ (see Appendix). Checking the sums thus obtained (Table I) against the values of $[t\mathrm{HT}]_0/2$ at the temperatures studied show that the deviations are (%) 5, 14, 49, and 34. It indicates that the model is correct and the data self-consistent and that mass balance is obtained.

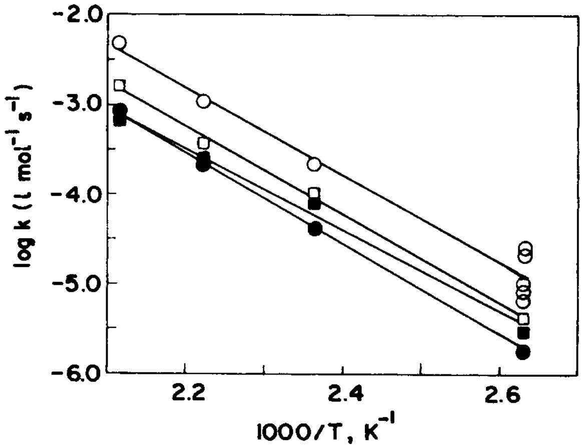


Figure 5. Log *k* vs. inverse temperature for the dimerization of *t*HT (○) and the formation of the three dimers a (●), b (□), and c (■).

TABLE I. Mass balance. The sum of the inverse intercepts of the plot $[D_i]^{-1}$ vs. time and the values of half the initial concentration of *trans*-hexatriene at the temperatures studied.

Temperature (K)	$\sum_i$ (intercept $_i$)$^{-1}$ mol/ℓ	$[HT]_0/2$ mol/ℓ
380	0.103	0.098
423	0.073	0.064
450	0.12	0.08
473	0.015	0.023

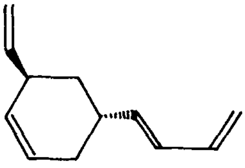
The rate for CHD dimerization was checked as well. The *endo* and the *exo* dimers rate coefficients are given in Figure 6 and below

$$\log k_{5a} = -(23{,}200 \pm 1500)/4.576\,T + (6.1 \pm 0.2)$$

$$\log k_{5b} = -(25{,}400 \pm 1500)/4.576\,T + (6.5 \pm 0.2)$$

These values are similar to those obtained previously [12].

The structures of dimers 3b and 3c were determined by ^{13}C-NMR and compared with published spectra [15]. The concentration of dimer 3a was too small to be analyzed. The structures of 3b and 3c and a possible structure of 3a are



3a dimer

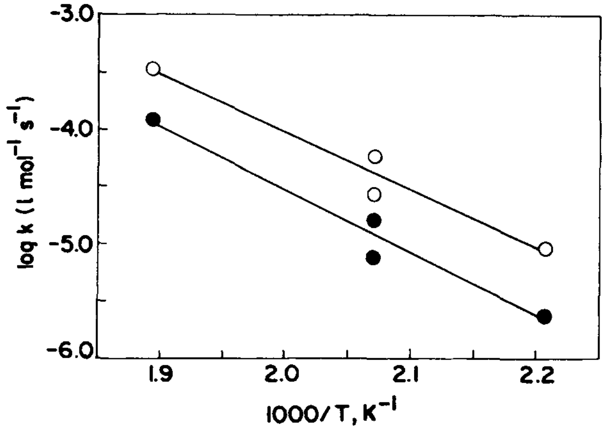
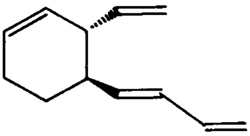
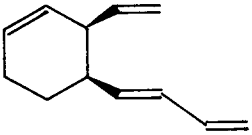


Figure 6. Log *k* vs. inverse temperature of cyclohexadiene dimerization, endo (○) and exo (●).



3b anti-3-vinyl-4-butadienylcyclohexene



3c syn-3-vinyl-4-butadienylcyclohexene

In summary, the thermal reactions of the isomerization of *cis*-hexatriene and the dimerization of both *cis* and *trans*-hexatriene were investigated in the liquid phase over the temperature range of 380 K–473 K. The rate coefficients for the various processes are reported and the structures of some of the dimers determined.

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Appendix

Determination of the individual rate coefficients for the disappearance of HT and appearance of the three dimers.

The reaction scheme for the disappearance of HT and appearance of the dimers is

$$\begin{aligned} 2\mathrm{HT} &\xrightarrow{k_1} D_1 \\ &\xrightarrow{k_2} D_2 \\ &\xrightarrow{k_3} D_3 \end{aligned}$$

The rate of disappearance of [HT] is

$$\text{(A1)} \qquad \frac{d(a-y)}{dt} = -2k(a-y)^2 = k'(a-y)^2$$

where a is the initial concentration of HT, y is the amount decomposing, and k is the overall rate coefficient for the decomposition of HT and t is the time. k is given by

$$\text{(A2)} \qquad k = \sum_{i=1}^{3} k_i$$

The integral expression for the concentration of HT is

$$[\mathrm{HT}] = a/(1 + ak't) \tag{A3}$$

The rate of appearance of dimer i is

$$\frac{d[D_i]}{dt} = k_i[\mathrm{HT}]^2 \tag{A4}$$

Substituting eq. (A3) in eq. (A4) and solving, the following is obtained

$$[D_i] = \frac{ak_i}{k'}\left(1 - \frac{1}{1 + ak't}\right) \tag{A5}$$

The sum of $[D]$ at infinite time is

$$\sum [D_i]^{\infty} = \sum_i \frac{a}{2}\frac{k_i}{k} = \frac{a}{2} \tag{A6}$$

Plots of $1/[D_i]$ vs. $1/t$ from eq. (A5) yield intercepts of $1/[D_i]_{1/t=0} = 2k/ak_i$. The sum of the inverse of the intercept yields therefore $a/2$ [eq. (A6)] which is half of the initial concentration of HT.

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