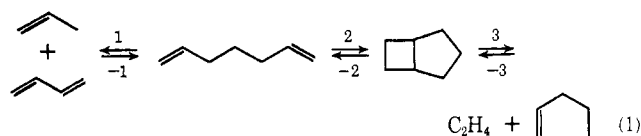# Thermochemical Kinetics of the Retro-"Ene" Reactions of Molecules with the General Structure (Allyl)XYH in the Gas Phase. 6.[1] The Concerted Unimolecular Decomposition of Hepta-1,6-diene

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Abstract: The kinetics of the thermal decomposition of hepta-1,6-diene (HD) have been studied in the gas phase over the temperature range 628–744°K. Propylene and butadiene in essentially equimolar concentrations are the major reaction products, with 4-methylcyclohexene, cyclopentene, and ethylene as minor detectable side products at large conversions. First-order rate constants for the disappearance of HD, obtained by an internal standard technique, fit the Arrhenius relationship, $\log k$, sec^{-1} = 11.31 ± 0.44 − (47.00 ± 0.73 kcal mol^{-1})/2.303RT. The reaction is homogeneous, and up to a 20-fold excess over HD of added but-1-ene, propylene, or toluene did not affect the rate constants. The entropy of activation derived from these data is $\Delta S^{\pm}$ = −11.3, in excellent agreement with prediction. The extent of nonsynchronous bond breaking and the nature of the transition state involved in these reactions is discussed. The reaction is best described as a concerted "retro-ene" elimination of propylene. The observed activation parameters are in line with a cyclic six-center transition state and with the results obtained for similar reactions of compounds of the general structure (allyl)XYH, where X equals NR, O, CO, or CR$_2$ and Y equals CR$_2$ or O.

An independent study of the kinetics of the thermal decomposition of hepta-1,6-diene (HD) has not been reported to date. Ellis and Frey,[3] when pyrolyzing bicyclo[3.2.0]heptane (BCH) observed a fast secondary reaction of the primary product HD, yielding propylene and butadiene in practically equimolar quantities.


$$C_2H_4 + \square \quad (1)$$

We have become interested in reaction 1 in connection with a series of investigations in this laboratory[4,5] of the thermochemical kinetics involved in reactions of the general type

$$\text{(allyl)XYH} \longrightarrow \diagup\diagdown + X{=}Y$$
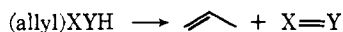
Based on these studies it was to be expected, that n,-(n + 5)-diolefins should in principle be capable of undergoing a concerted 6-center "retro-ene" decomposition in analogy with allyl alkyl ethers,[6] but-3-enoic acids,[7] but-3-enols,[8] and N-allyl-N-alkylamines.[4,5] Furthermore, the absence of a heteroatom should yield interesting information regarding the nonsynchroneity involved in these reactions, *i.e.*, the amount of charge separation in the six-center transition state. For

monoolefins (C$_5$ and higher) the possibility of the contribution of a concerted six-center reaction mechanism to the over-all pyrolysis, in competition with the radical path, *via*

$$\diagup\diagdown + {=}\diagup^R \quad (2)$$
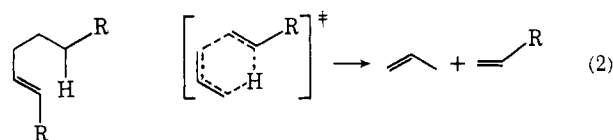
has been pointed out in the literature.[9-11] In the hepta-1,6-diene molecule, the allylic C–H bond to be partially broken in the transition state is, both on a homopolar or heteropolar basis,[12] considerably weaker than the corresponding bond in hept-1-ene. The concerted six-center decomposition path should then be facilitated in hepta-1,6-diene.

Experimental Section

Apparatus and Procedures. The high vacuum static reaction system and general procedures were the same as described earlier.[4,5,13] An experiment was started by injecting mixtures of HD with toluene through a silicon rubber septum into the heated deadspace situated immediately above the Pyrex reaction vessels. After 15 sec pressure equilibrium was always established. The initial and final pressures were recorded. The reaction was quenched by expanding the reaction mixture into a trap kept at liquid nitrogen temperature. Noncondensable gases were continuously removed *via* an automated Toepler pump.

The liquid condensate was then separated at −70° into a "light" fraction (containing mostly propylene + butadiene) and a residual "heavy" fraction (containing mostly HD + toluene). The gaseous light fraction was measured in a gas buret prior to analyses by glc. The glc analysis of the "heavy" product fraction was used as basis for the kinetic analyses of the system.

Materials. Toluene (T, used as an internal standard) was ob-

(1) Part 5: K. W. Egger and P. Vitins, *Int. J. Chem. Kinet.*, in press.

(2) Address correspondence to Chemical Laboratories, City of Berne, 3011 Berne, Switzerland.

(3) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4184 (1964).

(4) K. W. Egger, *J. Chem. Soc., Perkin Trans. 2*, 2007 (1973).

(5) (a) P. Vitins and K. W. Egger, *Helv. Chim. Acta*, 56, 17 (1973); (b) *Int. J. Chem. Kinet.*, in press; (c) K. W. Egger and P. Vitins, *J. Chem. Soc., Perkin Trans. 2*, submitted for publication.

(6) W. H. Richardson and H. E. O'Neal in "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., 1972, p 430.

(7) D. B. Bigley and R. W. May, *J. Chem. Soc., B*, 557 (1967).

(8) G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 7242 (1965).

(9) A. T. Blades and H. S. Sandhu, *Int. J. Chem. Kinet.*, 3, 187 (1971).

(10) W. Tsang, *Int. J. Chem. Kinet.*, 1, 245 (1969).

(11) W. Tsang, *Int. J. Chem. Kinet.*, 2, 23 (1970).

(12) K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, 56, 1516, 1537 (1973).

(13) K. W. Egger, *J. Amer. Chem. Soc.*, 89, 504 (1967).

tained from Fluka Chemical Corp., Buchs, Switzerland, and glc analysis showed it to be at least 99.66% pure with two major "light" impurities (4.26 and 4.67 min), which did not interfere with the product analyses. Hepta-1,6-diene (HD) was purchased from K & K Laboratories, Inc., Plainview, N. Y., and was found to be more than 99.5% pure based on glc analysis, with a major impurity peak immediately preceeding HD. n-Heptane used in two experiments as internal standard and obtained from U.C.B. Brussels was better than 99.6% pure. Propylene and but-1-ene, used as additives, were obtained from Fluka, with ~99.8% purity. The total amount of impurity observed by glc in the mixtures amounted to 0.65% and was taken into account in the analysis of the product mixture.

The starting mixtures had the following $[HD/T]_0$ ratios: B 0.5503, C 0.8838, and D 1.86. Mixture A used n-heptane (H) as internal standard in a ratio $[HD/H]_0 = 1.127$.

Analyses. Gas–liquid chromatographic analyses (glc) were carried out using a F&M model 810 gas chromatograph equipped with TC detectors and a Disc Integrator. A 4 m × 0.25 inch column, filled with Chromosorb W, containing a 33% (weight) coating of Carbowax 20M and operated with a helium flow of 100 cm^3 min^{-1} gave quantitative separation of the products. The following retention times (in minutes) were observed: light fraction at 55°: ethylene 0.28, propylene 0.83, butane 1.3, but-1-ene 1.86, butadiene 3.55, cyclopentene 4.00. Heavy fraction at 135°: cyclopentene 2.74, 1,6-heptadiene 4.22, 4-methylcyclohex-1-ene 7.10, toluene 16.69, and minor impurities in the product samples at 5.99 (impurity A), and 10.35 (impurity B).

Over a period of one month the reproducibility of over 25 analyses of the starting mixture B, used in most experiments, was observed to be 0.6043 ± 0.5% (standard deviation). The repro- ducibility of the product mixtures, carried out at least in duplicate, was usually better than 0.5%.

Noncondensable (liquid N_2) gases were analyzed using a 4-m silica gel column, operated at room temperature. Quantitative separation of H_2 from air and CH_4 was obtained. Nmr analyses served to identify the reaction products propylene, buta-1,3-diene, cyclopentene, 4-methylhexene, benzene, and toluene unambiguously.

Results

In the temperature range 628 to 744°K, hepta-1,6-diene (HD) decomposes to yield propylene and buta-diene as primary and major observable products.

4-Methylcyclohexene, ethylene, and cyclopentene were identified as secondary products. Minor amounts of cycloheptene, cyclohexa-1,3-diene, benzene, and toluene were only observable in experiments carried to very high conversions. Noncondensable gases nor- mally amounted to less than 2% and at the highest conversion up to 7% of the "light" product fraction. The noncondensable gases collected from two indepen- dent "preparative" experiments, carried to very large conversions, were shown by glc to consist mainly of methane besides a small amount of air. Hydrogen was not present in the sample in detectable quantities.

The van't Hoff relationship for the equilibrium 1 in eq 1 calculates[14,15] to log $K_{1,-1}$, atm = 6.74 − (16.1 kcal mol^{-1})/2.303RT, and the back-reaction k_{-1} can then be neglected as the reaction is thermodynamically irreversible.

First-order rate constants for the depletion of the HD, calculated on the basis of the internal standard method, are given in Table I together with the relevant experimental data. Toluene and, in two experiments, n-heptane were used as internal standards. No systematic variation in the rate constants with any of the observed reaction parameters is apparent. The initial

(14) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

(15) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

HD pressure ranged from 10 to 117 and the total pressure from 30 to 590 Torr, and the conversions at a given temperature bloc varied more than fivefold and ranged over-all from 3 to 75%. Excessive amounts (up to 20-fold) of propylene or but-1-ene added to the starting mixture, as well as the use of two different independent static reaction systems and reaction vessels of 1 and 2 l. volume, respectively, did not affect the rate constants.

The homogeneous nature of the reaction is demon- strated with consistent rate constants obtained, using a packed reaction vessel with a 14-fold larger surface to volume ratio.

Conversions based on pressure changes were between 30 and 77% of those based on the internal standard, and those based on the propylene yield ranged from 50 to 95% with an average at about 70%. The mass balances observed in experiments with large amounts of starting material and carried to purposely high conversions were normally within 10%, with an obvious loss in butadiene, and to a lesser extent in propylene. The ratio of propylene to butadiene observed in the "light" product fraction ranged from about 0.95 to 1.9, averaging at 1.4. Particularly careful distillation of the collected product mixture, obtained from low conver- sion experiments, always yielded closely equimolar concentrations of propylene and butadiene, in agree- ment with Ellis and Frey.[3] With larger conversion, the partial loss of butadiene and propylene is in line with the consistently low values for the pressure increases, and the formation of Diels–Alder products, such as 4-methylcyclohexene.

At low conversions the amounts of impurities ob- served in the product fractions were negligibly small. With larger conversions, however, substantial amounts of side products were found both in the "light" and "heavy" product fractions (compare Table I). In the light product fraction, ethylene was the dominant side product, amounting up to 30% of the propylene re- covered at the highest temperature and conversion. The amount of butenes observed never exceeded 3% of the propylene formed even under the most rigorous experimental conditions. Variable amounts of cyclo- pentene were also present in this fraction. Part of the cyclopentene was retained in the hepta-1,6-diene–toluene fraction. 4-Methylcyclohexene (MCH), the major impurity in the heavy product fraction, amounted up to 20% of the HD converted, in line with an increased loss of butadiene and propylene. The other two minor impurities A and B observed in the glc analysis of this fraction usually amounted to less than 20% of the MCH.

Least-squares analysis of the rate constants in Table I yields the Arrhenius relationship log k, sec^{-1} = 11.28 ± 0.18 − (46.90 ± 0.56 kcal mol^{-1})/2.303RT. The quoted errors are standard deviations. The *maximum* likely error in the activation energy[16] is calculated to 2.25 kcal mol^{-1}.

Disregarding the experimental data at the highest temperature bloc of 744°K, where high conversions and relatively large amounts of side products have been observed, results in activation parameters of 11.31 ± 0.44 for log A and 47.00 ± 0.73 for E_a. This is in good

(16) S. W. Benson, "The Foundations of Chemical Kinetics," Wiley, New York, N. Y., 1960, p 91.

Table I. The Kinetics of the Thermal Decomposition of Hepta-1,6-diene (HD) to Butadiene (BD) and Propylene (P)

Temp, °K	Starting material		Time, min	Conversion in % [HD]₀ᵇ	$k \times 10^{4},{}^{c}$ sec⁻¹	Side products	
	[HD]₀, Torr	[P_tot]₀,ᵃ Torr				C₂H₄ % of [P]_f	X % of [HD]₀
627.7	21.7	61.2	101	4.47	0.07539		
627.6	53.5	150.8	106	4.79	0.07722		
627.6	116.8	329	120	5.11	0.07286		
627.6	34.7	97.8	155	11.0	0.1247		
627.6	27.4	79.1	300	18.1	0.1107		
633.9 Pʰ	22.4	63.1	122	7.42	0.1053		
644.7	77.75	219	30	3.00	0.1691		
644.8	112.5	317	41	5.94	0.2488		
644.7	21.1	59.5	77	9.57	0.2178		
644.4	27.9	427.0ᵈ	101	14.1	0.2514		3.5
644.4	27.4	77.2	102	14.9	0.2628	3.5	4.2
665.2	7.54	50.9	20	9.38	0.8211		
665.2	10.3	29	26	11.4	0.7575		
665.2	22.8	64.3	30	11.4	0.6737		3.3
665.4	22.6	63.6	35	13.4	0.6860	2.6	
665.2	17.1	48.2	45	22.2	0.6970		2.8
665.4	35.2	587.9ᵉ	135	43.8	0.7118		
665.8 Pʰ	42.3	119	25	11.6	0.8203	~3	
688.8	42.2	119	11	15.1	2.358		
688.8	12.2	34.4	17	21.2	2.334		
688.8	23.4	65.8	25	32.7	2.642	8	
687.5	17.6	377.6ᶠ	40	40.7	2.1760		10.9
687.5	33.7	94.8	48	47.0	2.203		14.7
718.0	56.5	159.1	5	25.2	9.686		4.9
718.0	30.8	65.7 C	5.5	29.0	10.37		5.3
718.0	17.1	36.4 C	8.16	38.6	9.940		7.6
715.7	41.4	116.7	10.5	44.1	9.229		
720.7ⁱ	64.42	121.6 A	12	56.9	11.68	26	
719.6ⁱ	69.261	195.1 D	10	49.6	11.41	20	
720.8ⁱ	92.56	174.7 A	12	58.1	12.07	34	
715.7	46.4	130.7	15	56.6	9.279		
744.3ᵍ	13.0	36.5	2	32.8	33.11	16	
744.3ᵍ	31.5	88.6	2	33.9	34.46	16	
744.3ᵍ	12.8	36	2.3̄	30.8	26.27		11
744.3ᵍ	24.85	70	3	50.2	30.15		9.8
744.3ᵍ	31.2	87.9	3.5	50.1	33.13		11
744.3ᵍ	48.64	137	5.25	74.6	43.43	30	15

ᵃ For the composition of the starting mixtures indicated with A, B, C, and D compare the Experimental Section. Mixture B has been used in most experiments, indicated by the absence of a letter in this column. ᵇ Calculated from the gas chromatographic analyses based on the internal standard method. ᶜ Based on internal standard. ᵈ 348 Torr but-1-ene added. ᵉ 489 Torr but-1-ene added. ᶠ 328 Torr propene added. ᵍ Not used in computing the Arrhenius parameters. ʰ Packed reaction vessel. ⁱ Reaction system II with reaction vessel of 2148 cm³.
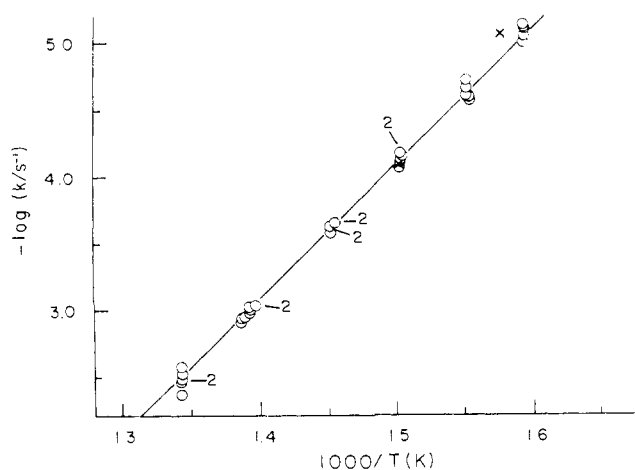

Figure 1. Arrhenius plot for the unimolecular thermal decomposition of hepta-1,6-diene; X and O indicate experiments carried out in packed and unpacked reaction vessels, respectively, and numerals indicate overlapping points.

agreement with the results obtained from the complete set of data. Figure 1 shows the Arrhenius plot of the rate constants.

Discussion

The apparently homogeneous decomposition of hepta-1,6-diene to propylene and buta-1,3-diene in the gas phase in the temperature range 628 to 744°K is essentially a clean process following first-order kinetics. The rate constants calculated using toluene or n-heptane as internal standard were found to be independent of pressure, the presence of more than a 20-fold excess of olefins, the conversion attained, or the reaction system and reaction vessels used. Except for high conversions, the amounts of side products are kinetically insignificant. The experimental data are perfectly consistent with the concept of a concerted retro-"ene" mechanism involving a six-center transition state as shown in eq 2. As outlined in the Appendix section, a first-order dependence in HD as well as the formation of propylene and butadiene as major products would in principle also be consistent with a radical decomposition path. Apart from the fact that the activation parameters observed are inconsistent with a radical scheme, the absence of significant amounts of hydrogen, butenes, and radical recombination products as well as the consistency of the observed rate constants in the

Table II. Activation Parameters for the Gas Phase Concerted Six-Center Retro-"Ene" Elimination of Propylene from Molecules of the General Structure (Allyl)XYH.

| Reactant | X | Y | $-\log A$, sec^{-1} | | | E_a, kcal mol^{-1} | $G(650)$, kcal mol^{-1} | Ref |
			Observed	Intrinsic[a]	Predicted[b]			
Allylcarbinols	CH₂	OH	11.65	11.65	11.7	41	6.3	18
	CH(CH₃)	OH	11.93	11.93	11.7	40.9	5.4	18
	C(CH₃)₂	OH	12.14	12.14	11.9	40.7	4.6	18
	C=O	OH	11.34	11.34	11.1	40.6	6.8	19
Allyl ether	O	C₂H₅			(11.7)	(44.7)	9.9	6
Allylamines	NH	C₆H₁₀	11.44	11.44	11.5	42.2	8.1	4
	NH	allyl	11.35	10.8	11.3	38.0	4.2	5b
	N(allyl)	allyl	11.74	10.9	11.5	38.3	3.3	5a
	NH	CH₃	11.52	11.0	11.4	44.0	9.7	5c
Olefins	CH₂	allyl	11.28	10.7	11.2	46.9	13.3	This work

[a] Corrected for path degeneracy. [b] Predicted value based on the method outlined in ref 17. Path degeneracy taken into account.

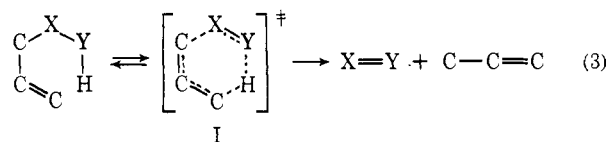Table III. Retro-"Ene" Decomposition Routes in Olefin Pyrolyses

| Olefin | Experimental conditions | | Products[b] | $\log A$, sec^{-1} | | E_a, kcal mol^{-1} | | % molecular[d] | Ref |
	System[a]	T, °K		Obsd	Est[c]	Obsd	Est		
Hepta-1,6-diene	S	650–750	BD, P	11.3	11.2	47.0		100	This work
Hept-1-ene	TCF	833–887	1-B, P (C₂H₄, CH₄, HD)	11.8[e]	11.0	54[f]	50.9[f]	?	9
Pent-1-ene	S	733	C₂H₄, P (CH₄, 1-B, BD)		11.2	49.9[f,h]		?	20
3,4-Dimethylpent-1-ene	SPST	1000–1100	2-B, P		11.6	50.3[g]		~10	10
4-Methylpent-1-ene	S	743–803	(C₂H₄, CH₄, HB, BD)		11.8	51.4[g]		?	21
4-Methylpent-1-yne	SPST	1100	Allene, P	13.1	11.7	59	51.9[f]	70	11
4-Methylhex-1-ene	TCF	839–889	1-B, P (CH₄, C₂H₄, HD)	12.2[e]	11.2	55[f]	51.1[f]	?	9
			2-B, P (CH₄, C₂H₄, HD)	12.0[e]	11.0	54[f]	50.1[f]		9

[a] S stands for static, SPST for single pulse shock tube, and TCF for toluene carrier flow systems. [b] Minor products are given in parentheses. 1-B and 2-B stand for 1- and 2-butene, respectively, BD for buta-1,3-diene, P for propylene, and HD for hexadiene. [c] Estimated data using the concept given in ref 17. [d] Contribution of the molecular path in percent of the over-all conversion observed. [e] Calculated values taken from ref 9. [f] Calculated on the basis of experimental data and estimated A factors. [g] Calculated from the experimental data for the radical reaction assuming $k_{\text{molecular}} = k_{\text{radical}}$, using a predicted $A_{\text{molecular}}$. These estimates are lower limits. [h] Appears to be a predominantly molecular decomposition reaction.

absence of any added olefins substantiate the assumption of a predominant concerted nature of the reaction.

The observed preexponential factor of 11.28 is in excellent agreement with a predicted value of 11.2 based on the method and the data given by O'Neal and Benson[17] and our estimates discussed in the Appendix section.

Table II summarizes the activation parameters for reactions of the general type shown in eq 3. The for-

$$
\underset{\underset{\text{C}}{\text{C}}\overset{\text{X}}{\diagdown}\underset{\text{H}}{\overset{\text{Y}}{\diagup}} \rightleftharpoons \left[\underset{\underset{\text{C}}{\text{C}}\overset{\text{X}}{\diagdown}\underset{\text{H}}{\overset{\text{Y}}{\diagup}} \right]^{\ddagger} \longrightarrow \text{X}=\text{Y} + \text{C}-\text{C}=\text{C} \quad (3)
$$

I

mation of the expected products propylene and X=Y, the good agreement between experimental and predicted values of the preexponential factors, and the relatively narrow range of the activation energies observed demonstrate the validity of the general reaction scheme 3 for the reactions listed in Table II.

The observed difference of 9 kcal mol^{-1} in E_a between hepta-1,6-diene and diallylamine, despite practical agreement in the dissociation energies of the C–X and

(17) H. E. O'Neal and S. W. Benson, J. Phys. Chem., 71, 2903 (1967).
(18) G. G. Smith and B. L. Yates, J. Chem. Soc., 7242 (1965).
(19) G. G. Smith and S. E. Blau, J. Phys. Chem., 68, 1231 (1964).
(20) R. Walsh, private communication, August 1973.
(21) M. Taniewski, J. Chem. Soc., 7436 (1965).

Y–H bonds involved[12] and the generally lower activation energies for molecules containing heteroatoms in the X or Y position, shows the potential for a pronounced polar character of the transition state I. The effects of substituents, the detailed nature of the transition state, and nonsynchroneity of the process is discussed in a forthcoming paper.[5c]

Having established the concerted six-center retro-"ene" mechanism and the activation parameters for the pyrolysis of hepta-1,6-diene, it appears appropriate to estimate the relative importance of this molecular path in the pyrolysis of monoolefins.

Based on the data for allylamines, listed in Table II, it is to be expected that the extra vinyl group bonded to the Y center (eq 3) reduces the Y–H bond dissociation energy (hetero- or homopolarly) thus reducing E_a. In case of a largely synchronous process, i.e., relatively little polar character in the transition state, anticipated for the olefin reaction, a considerably smaller vinyl substituent effect might be operative compared to that observed for amines (~6 kcal mol^{-1}). This appears indeed to be the case.

The available experimental data for the kinetics of the pyrolysis of olefinic compounds, which are in principle capable of undergoing a concerted retro-"ene" decomposition via (3), are listed in Table III. It should be noted, that for most olefins the concerted path is expected to be at best competitive with the radical decomposition path. As this work shows,

appropriate substitution can conceivably change the balance between the two processes. Reliable rate constants on olefin pyrolysis are scarce. Reasonably reliable Arrhenius parameters can only be obtained from the available data by taking mid-temperature rate constants and the estimated A factor. The preexponential factor for a 6-center retro-ene reaction can readily be estimated as outlined in the Appendix. The data show that the concerted decomposition route should in most cases at least be competitive with the radical process, contributing significantly to the over-all conversions observed in these systems. In the interpretation of experimental data on olefin pyrolysis, the molecular process should then always be considered very seriously.

The formation of ethylene and cyclopentene at high conversions and temperatures can be readily explained on the basis of a side reaction forming bicyclo[3.2.0]heptane (BCH) as an intermediate (compare eq 1). Ellis and Frey[3] studied the simultaneous decomposition of BCH into HD (k_{-2}) and into cyclopentene and ethylene (k_3). They reported log k_{-2}, sec^{-1} = 15.4 − 63.97/θ and log k_3, sec^{-1} = 14.84 − 60.74/θ. The equilibrium constant $K_{2,-2}$ has been estimated based on the data given in ref 22 and 23 to log $K_{2,-2}$ = 4.5 + 12/θ resulting in log k_2, sec^{-1} = 10.9 − 52.0/θ, where θ equals 2.303RT in kilocalories per mole. This work yielded log k_1, sec^{-1} = 11.31 − 47.0/θ resulting in k_1/k_2 = $10^{0.4+0.5/\theta}$, k_3/k_{-2} = $10^{-0.56+3.23/\theta}$, and k_3/k_2 = $10^{3.94-8.74/\theta}$. About one of 100 molecules would then be expected to form BCH which would decompose into cyclopentene plus ethylene about 20 times faster than it is formed. The experimental findings are then in good agreement with expectation based on these calculations. The small amounts of cycloheptene observed at high conversions also originate from BCH via the biradical formed in breaking the bridge bond.

The loss of the primary products buta-1,3-diene and to a lesser extent of propylene can be attributed to the Diels–Alder reactions of butadiene with propylene, but-1-ene, or HD, depending on the relative concentrations of these olefins in the reaction system. The product of the 4 + 2 addition of butadiene with propylene, 4-methylcyclohexene, has been identified by nmr and glc as the major isomeric impurity of hepta-1,6-diene. For details compare the Appendix.

In conclusion, it must be pointed out that the pyrolysis of n,(n + 5)-diolefins in general does not necessarily follow the reaction path outlined in this work for hepta-1,6-diene. Octa-1,6-diene and related compounds can undergo a six-center H-shifted cyclization reaction shown in eq 4. Involvement of both π bonds in the

(4)
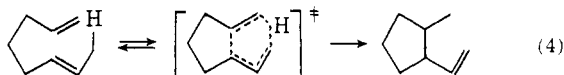
six-center transition state rather than one as is the case in the retro-"ene" reaction 3, should considerably lower the activation energy of the process. For octa-1,trans-6-diene activation parameters for (4) of E_a = 38.8 and log A, sec^{-1} = 9.90 at a temperature of 700°K

(22) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, 15, 266 (1970).
(23) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, No. 21 (1970).

have been observed.[24] Scaling the activation energy to a more reasonable, predicted A factor of $10^{10.4}$ results in $E_a \approx 41.0$ kcal mol^{-1}.

At 700°K, octa-1,6-diene would then isomerize about 15 times faster via (4) than decompose into propylene plus penta-1,3-diene via (3). Nevertheless, it is to be expected that the decomposition route will be kinetically important in these systems, as it is practically irreversible compared to the reversible isomerization reaction, which thermodynamically favors the cyclics by about a factor of 50 over the open-chain diolefin.

Appendix

1. Calculation of the Entropy of Activation and Preexponential Factor (Entropies Are Given in cal deg^{-1} mol^{-1}, 1 cal = 4.1859 J). Method and data, where not specified, are taken from ref 17.

(a) Symmetry, reaction path degeneracy = 4, $\Delta S_\sigma{}^{\ddagger}$ = R ln 4 = 2.77 eu.

(b) Vibration, bends = 2.2, stretches = −1.2, $\Delta S^{\ddagger}_{ring}$ (700°K) = 1.0 eu.

(c) Rotation (700°K) (for nomenclature compare ref 23).

Ground state S^0		Activated complex S^0		$\Delta S^{\ddagger}_{rot}$
(Ethyl — ∞)	8.4 →	$(CB2_{3e})_t$ = 3.5		−4.9
(n-Propyl-n-Bu)	7.7 →	reaction coordinate		−7.7
$(P_{4e})_t$	1.0 →	$(P_{3e})_t$	2.1	+1.1
(n-Propyl-n-Bu)	7.7 →	$(TB2_{3e})_t$	4.1	−3.6

$\Delta S^{\ddagger}_{rot}$ (700°K) = 15.1 eu, ΔS_{tot} (700) = ΔS_σ + $\Delta S^{\ddagger}_{vib}$ + $\Delta S^{\ddagger}_{rot}$ = 11.3 eu. This leads to a predicted A factor at an average temperature of 700°K of log A(700)$_{pred}$ = 13.67 + $\Delta S^{\ddagger}_{tot}$/4.58 = 11.2, which compares very well with the observed preexponential factor of 11.3.

2. Evaluation of the Radical Route. In the absence of additives the thermal decomposition of HD initiated by C–C cleavage can be expected to proceed as follows
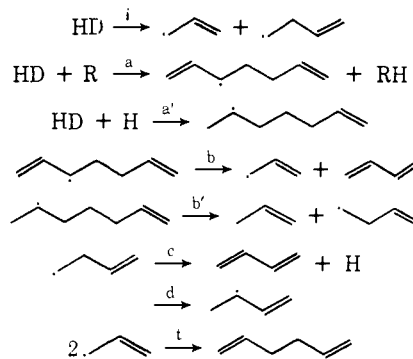
where R = or H

The products anticipated would be: propylene (P), butadiene (BD), butenes (B), hexa-1,5-diene, and possibly hydrogen. For a mean temperature of 700°K, log K_a, l. mol^{-1} sec^{-1} for the A radical can be estimated[25] at 8.2 − (8.3 kcal mol^{-1})/2.303RT and log

(24) W. D. Huntsman, personal communication, 1974.
(25) (a) A. F. Trotman-Dickenson and G. S. Milne, *Nat. Stand. Ref. Data Ser.*, *Nat. Bur. Stand.*, No. 9 (1967); E. Ratajczak and A. F. Trotman-Dickenson, "Supplementary Tables to Bimolecular Gas Reactions," University of Wales Institute of Science and Technology, 1969; (b) J. A. Kerr and E. Ratajczak, "Second Supplementary Tables of Bimolecular Gas Reactions," Department of Chemistry, University of Birmingham, 1972.

k_c, sec^{-1} at 13.7 − (32 kcal mol^{-1})/2.303RT.[12] For our experimental [HD] concentrations, ranging between 2.5 × 10^{-4} and 3 × 10^{-3} mol l.$^{-1}$, the ratio of the rate of abstraction (R_a) vs. hydrogen cleavage (R_c) is then given by R_a/R_c = 10$^{-5.5+(23.7 \text{ kcal mol}^{-1})/2.303RT}$. [HD]. R_a/R_c would then be expected to range between ~0.02 and 0.2, implying the predominant formation of butadiene via route c compared to the formation of butenes via a.

Isomerization reaction d is not expected to compete with route c. k_b can be estimated at ~10$^{14.5}$· 10$^{-20 \text{ kcal mol}^{-1}/2.303RT}$ and consequently $k_b \gg k_a$[HD].

As indicated in the reaction scheme three radicals can be expected as chain carriers, whereby H atoms are a special case apart from the allyl and butenyl radicals in that the addition to HD (reaction a') will be competitive with abstraction (reaction a). The Arrhenius expression for the former reaction[25] can be estimated as log k_a, 1. mol^{-1} sec^{-1} = 10.4 − (2.8 kcal mol^{-1})/RT and the latter[26] as log k_a, 1. mol^{-1} sec^{-1}) = 10.7 − (5.0 kcal mol^{-1} sec^{-1})/RT. Hence, at a mean temperature of 700°K, the ratio $k_{a'}/k_a$ = 2.43, implying that about 30% of the H atoms formed should react to yield H$_2$.

Experimentally H$_2$ is not found and the steady-state treatment does not lead to a simple first-order dependence in [HD] as observed.

In the presence of added hydrogen donors (but-1-ene and propylene) the following modified radical decomposition path would be expected.
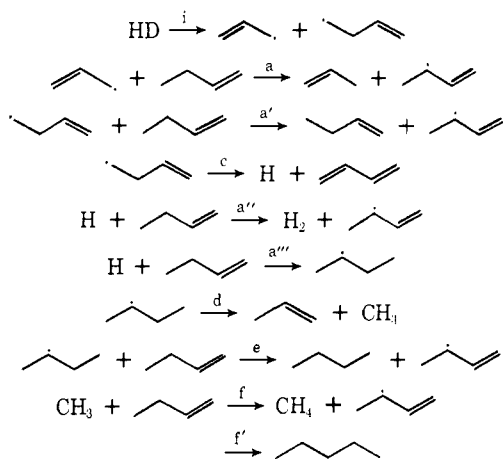
(26) (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **54**, 4662 (1971).

The Arrhenius expression for reaction d[26] is log k_d, sec^{-1} = 13.4 − (33.2 kcal mol^{-1})/RT and for reaction e can be estimated[25] as log k_e, 1. mol^{-1} sec^{-1} = 8.2 − (8.3 kcal mol^{-1})/RT. Hence, for the concentrations of [HD] used here, R_d/R_c = 85, and reaction e is negligible. It is also a well established fact[25] that H abstraction by CH$_3$ from an allylic position is considerably faster than addition to a carbon double bond, i.e., $k_f > k_{f'}$. Considering that H-atom addition to butene would be important, methane should be an expected product. In addition, an over-all first-order dependence in HD would be expected, with E over-all ≈ E_1 ≈ 69 kcal mol^{-1} and log A ≈ 15. The absence of the expected products and different Arrhenius parameters would therefore rule out a radical chain mechanism.

3. Estimation of the Activation Parameters for the Diels–Alder Reaction of Butadiene with Hepta-1,6-diene.
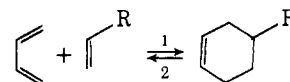
Based on the thermodynamic data for hepta-1,6-diene,[15] pentenylcyclohexene (calculated on the basis of the group additivity concept[15]), and butadiene,[14] the equilibrium constant $K_{1,2}$ is given by log $K_{1,2}$, 1. mol^{-1} sec^{-1} = −8.37 + (40.12 kcal mol^{-1})/2.303RT. For 4-methylcyclohexene forming propylene and butadiene, k_2 was reported[27] as log k_2, sec^{-1} = 15.1 − (66.6 kcal mol^{-1})/2.303RT. To a first approximation we can expect the same activation parameters for the butadiene plus hepta-1,6-diene system. When combined with the expression for the equilibrium constant $K_{1,2}$ given above, this yields for the addition reaction 1 log k_1, 1. mol^{-1} sec^{-1} = 6.73 − (26.5 kcal mol^{-1})/2.303RT. At the highest experimental temperature of 750°K and with [HD] ~ 2 × 10^{-3} mol l.$^{-1}$, the half-life (λ) of butadiene at an assumed 10% conversion would then still amount to about an hour. Taking the literature data for the ethylene plus butadiene[23] system rather than propylene plus butadiene as a basis results in λ ≈ 9 min. The addition reaction of two butadienes forming 4-vinylcyclohexene proceeds with about the same rate as ethylene plus butadiene. In the presence of excess hexa-1,3-diene or other olefins, this route can be disregarded.

Compared with these estimates the observed depletion of buta-1,3-diene appears to be too fast by about a factor of 10.

(27) W. Tsang, *J. Chem. Phys.*, **42**, 1805 (1965).