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Homogeneous Gas-Phase Decyclization of Tetralin and Benzocyclobutene

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Abstract: Tetralin has been decomposed in single pulse shock tube experiments in the temperature range of 1000–1400 K. The initial unimolecular decomposition channels involve the formation of benzocyclobutene and *o*-allyltoluene. Benzocyclobutene decomposes to form styrene. The main products from the hydrogen atom induced decomposition of tetralin are dihydronaphthalene, styrene, indene, and naphthalene. The following rate expressions have been determined: $k(\text{tetralin} \rightarrow \text{ethylene} + \text{benzocyclobutene}) = 3.5 \times 10^{15} \exp(-40\,003/T)\ \text{s}^{-1}$, $k(\text{tetralin} \rightarrow o\text{-allyltoluene}) = 1.2 \times 10^{15} \exp(-40\,111/T)\ \text{s}^{-1}$, $k(\text{benzocyclobutene} \rightarrow \text{styrene}) = 1.2 \times 10^{15} \exp(-37\,396/T)\ \text{s}^{-1}$, $k(\text{H} + \text{tetralin} \rightarrow \text{H}_2 + 4\text{-phenylbutyl radical}) \geq 0.55 \times k(\text{H} + \text{mesitylene} \rightarrow o\text{-xylene} + \text{CH}_3)$. Comparisons are made with published results from laser-powdered pyrolysis and shock tube studies, and it is concluded that in both cases initial unimolecular channels are accessed. The temperatures in the laser experiments are at least as high in the shock tube studies. The rate expressions for tetralin decomposition are compatible with a biradical mechanism and follow the general patterns for related cyclic compounds.

This paper is concerned with the mechanisms and rates of decomposition of tetralin. In the course of this work we have also obtained information on the stability of benzocyclobutene. Tetralin has long been regarded as prototypical of the hydroaromatic structures in coal.[1] It is also widely used as hydrogen donor in studies bearing on coal liquefaction. As a result there has been a great deal of previous work on its chemical and thermal stability. This involve studies in liquid and gas phases and in flow and static systems. In the gas phase, thermal decomposition leads to production of naphthalene and 1,2-dihydronaphthalene, while in the liquid phase, ring contraction is an important process. The mechanisms for the formation of these products are uncertain. Rate constants for decomposition are difficult to relate to elementary processes.

Table I. Relative Product Yields from the Laser-Induced Decomposition of Tetralin at Lowest Energy Input

	direct photolysis	SiF_4 sensitized photolysis
benzoycyclobutene	72.6	58.5
styrene	11.7	8.3
o-allyltoluene	3.4	20.8
indene	4.2	0.2
1,2-dihydronaphthalene	6.2	10.3
naphthalene		

Laser pyrolysis experiments[2] using direct and sensitized (SiF_4) photolysis and extensive product and isotope labeling studies have been carried out several years ago. The sensitized decomposition is expected to approximate the thermal situation, and it was concluded that the main decomposition process involves benzocyclobutene formation. Another important initial product was *o*-allyltoluene. These are rarely detected in static or flow studies. 1,2-Dihydronaphthalene was found in small yields. From isotope labeling experiments it is clear that only very small quantities could have been formed from direct H_2 elimination. A variety of other products such as styrene, indene, and naphthalene was also detected. These were considered secondary products. On this basis

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(1) Poutsma, M. L. *A Review of Thermolysis Studies of Model Compound Relevant to Processing of Coal*; ORNL/TM-10673, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

(2) Comita, P. B.; Berman, M. R.; Moore, C. B.; Bergman, R. G. *J. Phys. Chem.* **1981**, *85*, 3266.

Table II. Rate Expressions for the Decomposition of Cyclanes and Related Compounds

rate expressions	ref
k(cyclobutane → 2-ethylene) = $4 \times 10^{15} \exp(-31\,500/T)$ s^{-1}	6
k(cyclopentane → 1-pentene) = $1.2 \times 10^{16} \exp(-42\,700/T)$ s^{-1}	4
k(cyclopentane → cyclopropane + ethylene) = $2 \times 10^{16} \exp(-42\,700/T)$ s^{-1}	4
k(cyclohexane → 1-hexene) = $5 \times 10^{16} \exp(-44\,400/T)$ s^{-1}	5
k(cyclohexene → 1,3-butadiene + ethylene) = $1.4 \times 10^{15} \exp(-33\,500/T)$ s^{-1}	7
k(hexane → 2-propyl) = $2.5 \times 10^{16} \exp(-41\,000/T)$ s^{-1}	7
k(1-pentene → allyl + ethyl) = $8 \times 10^{15} \exp(35\,600/T)$ s^{-1}	7
k(n-propylbenzene → benzyl + ethyl) = $3 \times 10^{15} \exp(-36\,000/T)$ s^{-1}	8

it was suggested that in the older studies the true thermal reactions were masked by surface-induced and chain decomposition processes. A summary of the relative product yields from the laser experiments can be found in Table I.

The temperature and time history generated under laser pyrolysis is uncertain. In the direct photolysis one cannot talk about the temperature at all. In the induced decomposition the general situation probably approximates thermal excitation. Rate expressions were not obtained. If thermal rate expressions are known however, the distribution of products can yield information on the reaction conditions. We have carried out such a study in the case of 1,2-dichloropropane leading to very informative results.[3] In that case, all four decomposition channels involve stable molecular species. The isotope labeling experiments of Comita et al.[2] show evidence of hydrogen atom induced decomposition. This complicates the interpretation of the results.

Earlier, we carried out studies on the mechanisms and rates of decyclization of intermediate-sized ring compounds.[4,5] An important focus of this study is the effect on the mechanisms and rates of decomposition of a cyclic molecule when it is bonded directly to a benzene ring. The prototypes for comparison are the decomposition of six- and four-membered ring compounds. The mechanisms and rate expressions for the thermal unimolecular decomposition of these compounds are well established.[4-7] Some earlier results and related information are summarized in Table II. In the case of cyclohexene and cyclobutane, the important issue is whether the reaction is concerted or if a biradical intermediate is involved. For cyclopentane and cyclohexane, the higher activation energies and slightly lower A-factors compared to bond-breaking reactions are inconsistent with concerted processes. Thus a biradical mechanism is operative. These bond-breaking reactions are of particular interest when compared to those involving noncyclic systems since there are severe constraints on the motions of the radical sites with respect to each other.

The key quantitative measure of the thermal stability of a molecule is the high pressure rate expression for unimolecular decomposition. The A-factor being related to the transition-state structure, and the activation energy defines its position on the energy scale. For both tetralin and benzocyclobutene decomposition such information does not exist. It should be noted that the values of the rate parameters yield mechanistic information, since, as noted earlier, the activation energy can be compared with known bond strengths. Figure 1 gives values of the bond strengths for the various linkages in tetralin.

Single pulse shock tube studies have unique capabilities for determining the mechanisms and rate constants for the decomposition of large organic molecules. This is due to the short reaction time and through gas chromatography the possibility of working at very low concentrations of reactants. Surface and chain reactions can be completely eliminated. True thermal unimolecular rate constants are being measured. The heating time, on the order of 500 μs, ensures that under the usual reaction pressures of several atmospheres the total number of collisions is on the order of 5×10^6. This is sufficient to assure a meaningful temperature.

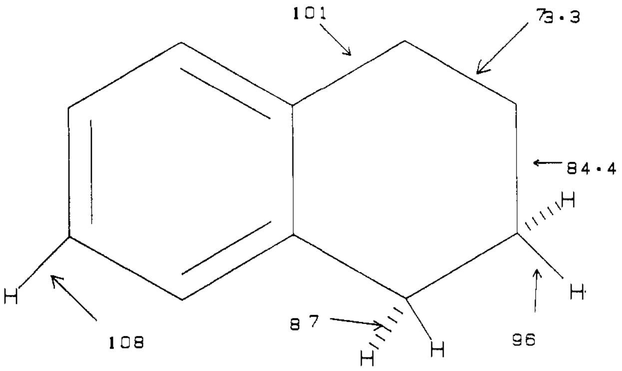

Figure 1. Estimated activation energies for bond breaking (kcal) in tetralin.

The limited number of collisions represents an absolute guarantee of the suppression of chain processes. With target molecules at the 100-ppm level or lower and with a hydrocarbon scavenger at factors of 100–1000-fold in excess, reactive radicals such as hydrogen atoms are converted into polyatomic organic radicals. These are in general much less reactive. As a result there is not sufficient time for reaction with the target molecule that is present in such low concentrations. Thus practically any hydrocarbon compound whose induced decomposition product is not a hydrogen atom can be used as a radical scavenger. In earlier studies we have used toluene and other methylated benzenes to convert hydrogen atoms into benzyl structures. These can only combine under our conditions to form dibenzyl or benzyl type compounds during and after the heating period. Here we use methane as the scavenger, and the resulting methyl radicals can also only recombine. The greater reactivity of methyl in comparison to that of the benzyl radical means that with methane, the scavenger to reactant ratio should be in the range of 1000:1 and the reactant concentration should not exceed 100 ppm under our conditions. These are the conditions for the first set of experiments. As it turned out the results were not critically dependent on these factors, so in subsequent measurements the conditions were relaxed. All these claims are in accord with published values of rate constants for abstraction processes and more important can be tested by varying relative concentrations of inhibitors and reactants.[9] For example, the rate constant for methyl attack on ethane is 10^8 L/mol-s at 1400 K. With ethane at a 100-ppm level in a total pressure of 2 atm, this leads to a lifetime of methyl radicals of 6 ms or an order of magnitude longer than the heating time. It is thus possible to isolate the initial unimolecular decomposition step for study. A more detailed discussion can be found in a review paper.[7]

Recently, we have extended the range of possibilities by studying the mechanisms and rates of H-atom attack on organic substrates in single pulse shock tube experiments. This involves the decomposition of trace quantities of a labile hydrocarbon such as hexamethylethane in the presence of large quantities of a more stable substrate (which does not decompose under the reaction conditions) and then the deduction of the desired information through a careful analysis of the reaction products.[10] We have established the mechanism and rate expressions for hexamethylethane decomposition as

$$k(\mathrm{HME} \rightarrow 2\mathrm{tC_4H_9} \rightarrow 2\mathrm{iC_4H_8} + 2\mathrm{H}) = 3 \times 10^{16} \exp(-34500/T)\ \mathrm{s^{-1}}$$

Thus from the yields of isobutene we establish the number of hydrogen atoms released into the system and also can calculate

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(3) Tsang, W.; Walker, J. A.; Braun, W. *J. Phys. Chem.* **1982**, *86*, 719.

(4) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 599.

(5) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 1119.

(6) Genaux, C. T.; Kern, F.; Walters, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 6196.

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

(9) Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087.

(10) Robaugh, D.; Tsang, W. *J. Phys. Chem.* **1986**, 90, 4159.

Table III. Experimental Mixtures Used in Studying Tetralin Decomposition

10% CH_4, 100 ppm tetralin in argon
10% CH_4, 50 ppm tetralin in argon
0.5% tetralin, 50 ppm hexamethylethane in argon
9.6% CH_4, 500 ppm tetralin, 100 ppm 1-methylcyclohexene in argon
8.3% CH_4, 2200 ppm tetralin, 86% 1-methylcyclohexene in argon

the reaction temperature. In this study we will be using this method as a probe to determine the contributions from chain pathways as opposed to the products from the direct unimolecular channels. The yields of the latter will be unaffected by induced decomposition processes. This procedure has been successfully employed in an earlier study.[5]

The use of an internal standard to determine the reaction temperature leads to the derivation of extremely accurate rate expressions, since the alternative method, where the temperature is derived from the gas dynamic properties of the shocked gas and the shock velocity leads to uncertainties in reaction temperatures of the order of 3–5% and thus to errors in rate expressions that are not acceptable for quantitative kinetics purposes. The general procedures have been successfully used for determining the thermal stability characteristics of many organic compounds.[7]

Experimental Section

The experiments are carried out in our heated single pulse shock tube where the temperature is maintained at 110 °C. The associated gas handling system is also maintained at this temperature. Under these conditions we have no problems in extracting from our shock tube compounds such as dibenzyl (boiling point, 251 °C). The mixtures that are used in these studies are summarized in Table III. Analysis of the final products is by gas chromatography with flame ionization detection. The columns used in the analysis are 30 m × 0.53 mm polydimethylsiloxalane and polyethylene glycol capillary columns operated in the programmed temperature mode.

Methane is used as the scavenger because tetralin is a very stable molecule. The rate constants for decomposition of tetralin at our temperatures are probably within an order of magnitude of that of the methylated benzenes that we have used as scavengers. Since the main mode of decomposition of such scavengers is via C–H bond split, this can introduce an extraneous source of reactive hydrogen atoms which will confuse the data analysis. Methane is stable under our reaction conditions. An added benefit in not using toluene or other methylated benzenes is that tetralin is also a large aromatic hydrocarbon. Its decomposition products may well be masked by the induced decomposition products from the scavenger during the course of our gas chromatographic analysis. On the other hand, the use of enormous quantities of methane makes it virtually impossible to determine to use the yields of C_1 and C_2 hydrocarbons as markers for extent of reaction. For the present study all our conclusions are based on the yields of the aromatic products. The tetralin and hexamethylethane were obtained from Aldrich Chemicals.[11] Gas chromatographic analysis did not reveal any significant impurities in the tetralin. The argon was of ultrapure grade and was obtained from Matheson. All the products except benzocyclobutene were identified on the basis of retention times with use of pure samples. We identified benzocyclobutene by thermally decomposing a known source, α-chloro-*o*-xylene.[12]

Table IV. Product Distribution (100 t $(conc)_f/(tetralin_i)$ from Tetralin Decomposition at High Dilutions and in the Presence of Large Excesses of Methane

temp	benzocyclobutene	styrene	*o*-allyltoluene	*o*-methylstyrene	indene	1,2-dihydronaphthalene	naphthalene	tetralin
				100 ppm Tetralin in 10% CH_4				
1260	2.68	0.126	0.75	0.037	0.082			93.8
1278	4.04	0.251	1.12	0.174	0.254		0.12	91.8
1292	5.0	0.47	1.51	0.08	0.265	0.66		91.7
1296	5.99	0.562	1.63	0.356	0.424			91.6
1324	10.0	1.72	2.56	0.816	0.847			83.6
1340	11.7	3.24	3.45	0.98	1.217	2.75	0.90	74.4
1344	13.3	3.95	3.02	1.03	1.11		0.95	71.1
1367	15.3	8.53	4.43	1.82	2.38	2.80	0.90	55.8
				50 ppm Tetralin in 10% CH_4				
1292	5.55	0.412	1.48	0.128	0.148			88.2
1302	7.45	0.861	1.93	0.228	0.193			86.3
1326	10.7	1.65	2.63	0.367	0.513			76.4
1344	13.0	4.23	3.23	1.39	1.33			74.2
1360	16.2	6.79	3.40	1.03	1.43		0.85	58.8
1375	18.3	10.1	3.36	0.94	1.52			59.0

Table V. Product Distribution Per Hydrogen Atom $(conc)_f/(isobutene)$ from the Hydrogen Atom Induced Decomposition of Tetralin[a]

temp	styrene	indene	methylindenes or methylindane		naphthalene	1,2-dihydronaphthalene	benzocyclobutene	*o*-allyltoluene
			50 ppm Hexamethylethane in 0.5% Tetralin					
1007	0.78	0.47					0.025	
1025	0.83	0.47	0.34	0.26	0.16	4.2		
1046	1.13	0.70					0.028	
1046	1.22	0.80	0.65	0.55	0.20	6.1		
1061	1.18	0.77					0.030	0.01
1078	1.18	0.77					0.032	0.01
1110	1.26	0.77	0.60	0.35	0.35	5.3		
1120	1.18	0.94					0.051	0.017
			50 ppm Hexamethylethane in 0.5% Tetralin and 0.6% 1,3,5-Trimethylbenzene[b]					
1014 (0.39)	0.18							
1014 (0.39)	0.18							
1029 (0.40)	0.18							
1068 (0.40)	0.18							
1107 (0.40)	0.18	0.15					0.055	
1113 (0.39)	0.18	0.15						

[a] The hydrogen atom source is hexamethylethane decomposition via the reaction $(tC_4H_9)_2 \rightarrow 2tC_4H_9 \Rightarrow$ 2isobutene 2 2H. Temperature calculated from rate expression for $k(tC_4H_9)_2 \rightarrow 2tC_4H_9) = 3 \times 10^{16} \exp(-34\,500/T)$ s^{-1}. [b] Number in parentheses refers to *m*-xylene from the induced decomposition of 1,3,5-trimethylbenzene.

Results

Table IV contains a summary of the data on the product distribution formed as a result of the decomposition of dilute quantities of tetralin in large excesses of methane at the higher temperatures. The major reaction products are benzocyclobutene, *o*-allyltoluene, and styrene. It can be seen that about 85% of the products have been recovered. Note also that the relative concentration of the major products is unchanged despite a factor of two decrease in tetralin to methane concentration. The implication is very strong that the major products that we have detected are derived directly or from a sequence of unimolecular processes. The temperature required to effect decomposition is higher than that required for the decomposition of large alkanes and is suggestive of the high degree of thermal stability of tetralin. The relative concentration of the minor products, indene, *o*-methylstyrene, and naphthalene show larger scatter. We are uncertain regarding the origin of this discrepancy. Part of this is probably an experimental artifact, since these compounds are present in small amounts, and accurate concentration measurements are rendered difficult by overlapping peaks. Significant quantities of 1,2-dihydronaphthalene was found. These may be due to a direct 1,2-elimination of H_2. However, the temperatures are sufficiently high that this can also be due to the cleavage of a C–H bond directly or, since it is not a major channel, through abstraction by methyl radical followed by the ejection of the hydrogen β to the radical site. There are similar ambiguities with respect to the other minor products, indene and *o*-methylstyrene. That is, we are uncertain as to their mode of production. From the induced decomposition studies, to be discussed subsequently, where indene is an important product, very little *o*-methylstyrene was detected.

The yields of styrene in these studies are particularly interesting. It can be seen that the temperature dependence is extremely strong. Thus, for example, from the reactions with 100 ppm tetralin in 10% methane the variation in benzocyclobutene yields was only a factor of 5, while that for styrene was a factor of 30 or more. This extremely strong dependence in temperature implies either an impossibly large activation energy and A-factor for a unimolecular process or that styrene is formed from the unimolecular decomposition of a product. Since it is well-known that the decomposition of benzocyclobutene leads to styrene formation, our observation is consistent with such a mechanism, and we will treat our data in this manner. At the higher temperatures, the *o*-allyltoluene also appears to decompose. This can be seen from the decrease in the ratio of the concentrations of *o*-allyltoluene to the sum of that of styrene and benzocyclobutene. It will be seen subsequently that at lower temperatures the activation energies for benzocyclobutene and *o*-allyltoluene formation are equal. We are uncertain of the nature of this decomposition process.

In order to get a better handle on chain contributions we carry out additional experiments in which trace quantities of hexamethylethane is decomposed in large excesses of tetralin. The former is much less stable than the latter, hence the much lower reaction temperature. The results are summarized in Table V. It can be seen that 1,2-dihydronaphthalene is the major product. Significant quantities of styrene, indene, methylindene, and naphthalene are important products, while the yields of benzocyclobutene and *o*-allyltoluene, the major products in the inhibited decomposition, are much smaller. The radical-induced nature of this decomposition can be seen from the change in yields when an inhibitor such as mesitylene is added to the reaction mixture at a concentration level close to that of the tetralin. The concentration of the two detectable major products are now reduced drastically. The presence of large amounts of mesitylene made measurements of the concentration of the other products impossible. This is consistent with reactive radicals attacking mesitylene and forming benzyl type radicals which under our reaction condition does not have sufficient time to attack tetralin. Evidence for H atoms reacting with mesitylene is furnished by the production of *m*-xylene. The relative yields of benzocyclobutene are unchanged despite the addition of the inhibitor. This demonstrates that it is not the result of radical-induced decomposition.

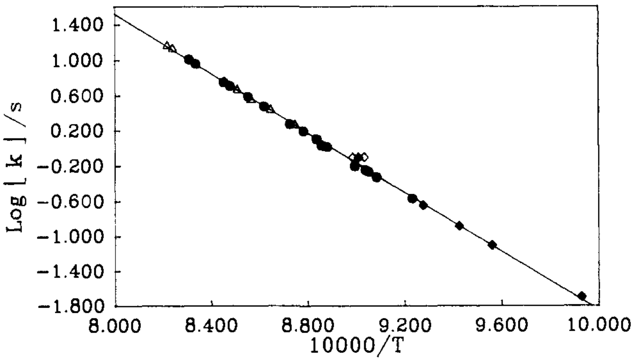

Figure 2. Arrhenius plot for the formation of benzocyclobutene from the decomposition of tetralin: 9.6% CH_4, 500 ppm tetralin, 100 ppm 1-methylcyclohxene in argon (△); 8.3% CH_4, 2200 ppm tetralin, 86% 1-methylcyclohexene in argon (●); 50 ppm hexamethylethane in 0.5% tetralin (◆); 50 ppm hexamethylethane in 0.5% tetralin and 0.6% 1,3,5-trimethylbenzene (◇). Pressures are 2–3 atm.

We next proceed to determine the rate expressions for benzocyclobutene and *o*-allyltoluene formation from tetralin decomposition. We could have in fact used the data given in Table V. However, the difference in rate constants between hexamethylethane and tetralin decomposition is extremely large, and the presence of all the other products in large quantities may lead to some uncertainties. We have carried out studies in the range of inhibitor to tetralin concentrations that is intermediate between the two extreme cases given in Tables IV and V. It should be noted that having established that benzocyclobutene and *o*-allyltoluene are not chain decomposition products we can now carry out experiments with smaller scavenger to reactant ratios. This is merely a matter of experimental convenience. In addition, we use, as an internal standard, the decomposition of 1-methylcyclohexene. It decomposes through a reverse Diels–Alder mechanism with the rate expression

$$k(\text{1-methylcyclohexene} \rightarrow \text{isoprene} + \text{ethylene}) = 10^{15} \exp(-33\,500/T)\ \text{s}^{-1}$$

This can be converted to a reaction temperature, *T*, from the relation

$$k = 10^{15} \exp(-33\,500/T) = \ln(1 - (\text{isoprene}/(\text{1-methylcyclohexene})_i))/t$$

where *t* is the heating time of 500 μs.

Figures 2 and 3 are Arrhenius plots for the rate constants of the formation of benzocyclobutene and *o*-allyltoluene from tetralin decomposition. The rate constants are obtained from the expression

$$k(\text{product}) = (1/t)(\text{product})/(\text{tetralin})_i$$

where the products are either benzocyclobutene or *o*-allyltoluene, and *t* is as before the heating time of 500 μs. The rate relationship is written in this form because in these studies tetralin conversion never exceeded 2%. The ratio of tetralin to the methane inhibitor was varied by a factor of 4. As expected there are no effects on the Arrhenius plot. Also included in Figure 2 are the data on benzocyclobutene formation from tetralin decomposition in the studies where we observed the effects of hydrogen-induced decomposition. In this case the temperature was determined from the yield of isobutene from hexamethylethane decomposition. Note that the results fall exactly on the line from the experiments with 1-methylcyclohexene decomposition. This is an additional and most striking quantitative demonstration that benzocyclo-

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(11) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation of endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment is necessarily the best available for the purpose.

(12) Loudon, A. G.; Maccoll, A.; Wong, S. K. *J. Am. Chem. Soc.* **1969**, *91*, 7577.

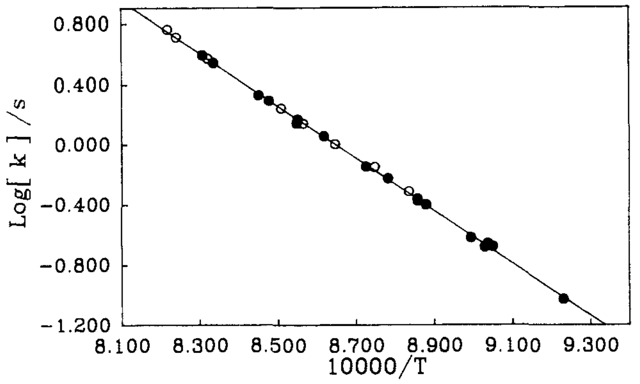

Figure 3. Arrhenius plot for the formation of *o*-allyltoluene from the decomposition of tetralin: 9.6% CH_4, 500 ppm tetralin, 100 ppm 1-methylcyclohexene in argon (○); 8.3% CH_4, 2200 ppm tetralin, 86 ppm 1-methylcyclohexene in argon (●). Pressures are 2–3 atm.

butene does not arise from a hydrogen atom induced decomposition. Least-squares treatment of the data lead to the following rate expressions for the two decomposition processes:

$$k_a = k(\text{tetralin} \rightarrow \text{benzocyclobutene} + \text{ethylene}) = 3.5 \pm 0.9 \times 10^{15} \exp(-40003 \pm 250/T)\ \text{s}^{-1}$$

$$k_d = k(\text{tetralin} \rightarrow o\text{-allyltoluene}) = 1.2 \pm 0.3 \times 10^{15} \exp(-40111 \pm 220/T)\ \text{s}^{-1}$$

Note the very small standard deviations. This is due to the use of the internal standard, and the errors are simply that due to the chromatographic analysis. In calculating the rate expression for benzocyclobutene formation we have not made use of the results from the induced decomposition studies since these are based on a different internal standard and in principle can lead to the introduction of systematic errors. Of course from Figure 2 it can be seen that this is not a problem. In Figure 3, we have not included the data from the induced decomposition. An examination of the data on Table V will demonstrate that had we plotted the results the fit would have been just as good as that for benzocyclobutene formation.

Figure 4 represents similar Arrhenius plots based on the yields of the styrene, indene, naphthalene, and 1,2-dihydronaphthalene. It can be seen that there is direct dependence on the relative ratio of inhibitor to tetralin and implies important contributions from radical-induced decompositions. The 1,2-dihydronaphthalene data show an unusual amount of scatter. We have no explanation for this effect.

We next consider the conversion of the benzocyclobutene to styrene. Our analysis is carried out on the assumption that the sole product from benzocyclobutene decomposition is styrene and is based on the data given in Table IV. Since benzocyclobutene is the reaction intermediate, then on the basis of the mechanisms as postulated in Figure 5, we find the ratio in styrene to benzocyclobutene + styrene concentrations to be related to the rate constant for tetralin and benzocyclobutene decomposition by the relation

$$\text{styrene}/(\text{styrene} + \text{benzocyclobutene}) = 1 - \{k_aQ/(k_b - k_aQ)\}[\exp(-qk_at) - \exp(-k_bt)]/[1 - \exp(-Qk_at)]$$

where $Q = 1 + k_d/k_a$, t is the residence time of 500 μs, and k_a is the rate constant for benzocyclobutene formation from tetralin and is determined from the relation

$$k_a = (1/t)\ln(1 - [(\text{benzocyclobutene} + \text{styrene})^*X/(\text{tetraline})_i])$$

where

$$X = 1 + \sum_i \text{products}_i/[\text{benzocyclobutene} + \text{styrene}]$$

For the present purposes the summed term is taken to be 0.65. This is the number that can be derived from the requirement of material balance at the higher extents of tetralin destruction. At lower conversions it becomes progressively less important. Thus any errors so introduced will not be significant. k_b is the rate constant for styrene formation. k_d is the rate constant for the formation of *o*-allyltoluene and from our earlier result can be taken as $k_d = 0.3k_a$. In an earlier section we have shown that

$$k_a = k(\text{tetralin} \rightarrow \text{benzocyclobutene} + \text{styrene} + \text{ethylene}) = 3.5 \times 10^{15} \exp(-40003/T)\ \text{s}^{-1}$$

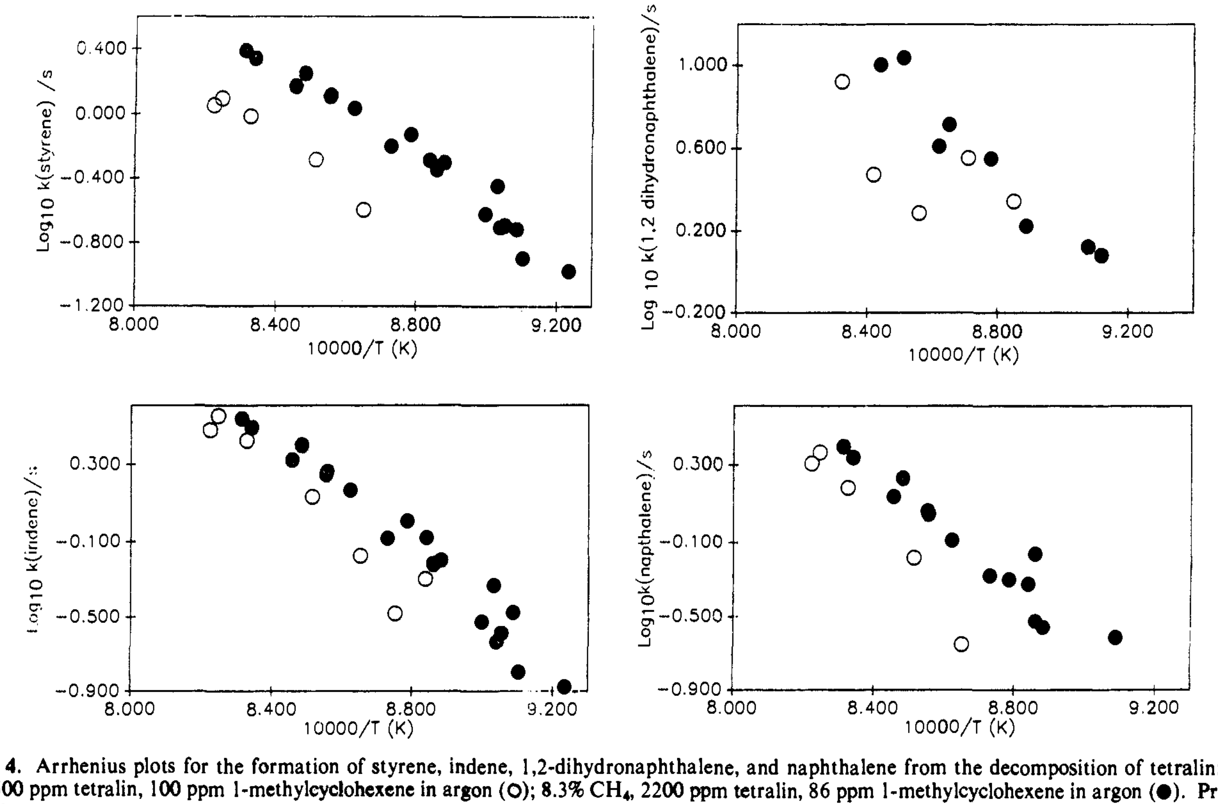

Figure 4. Arrhenius plots for the formation of styrene, indene, 1,2-dihydronaphthalene, and naphthalene from the decomposition of tetralin: 9.6% CH_4, 500 ppm tetralin, 100 ppm 1-methylcyclohexene in argon (○); 8.3% CH_4, 2200 ppm tetralin, 86 ppm 1-methylcyclohexene in argon (●). Pressures are 2–3 atm.

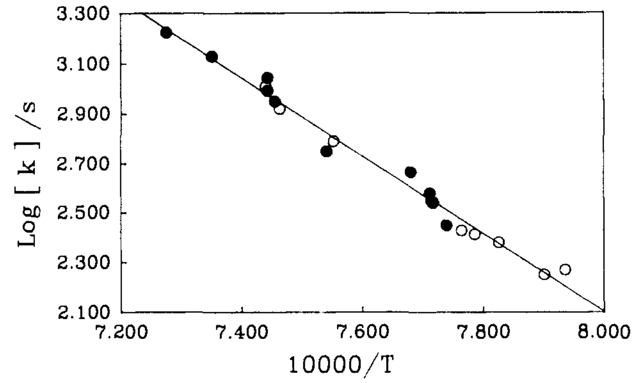

Figure 5. Arrhenius plot for the formation of styrene from benzocyclobutene decomposition: 10% CH_4, 100 ppm tetralin in argon (○); 10% CH_4, 50 ppm tetralin in argon (●). Pressures are 2–3 atm.

Thus having determined the value for k_a we can also calculate a reaction temperature. The Arrhenius plot of the results can be found in Figure 4. As before it can be seen that changing inhibitor to reactant concentration has a minimum effect. The rate expression consistent with this plot is

$$k_b = k(\text{benzocyclobutene} \rightarrow \text{styrene}) = 1.2 \times 10^{15} \exp(-37396 \pm 1100/T)\ \text{s}^{-1}$$

The data have considerable more scatter than that for the direct tetralin pyrolysis products. This is due to its being a secondary process, and the errors in the rate constant for the initial process are factored into the analysis. In addition there is also a contribution from a small imperfectly resolved *o*-xylene peak that was at the foot of the styrene peak.

The data in Table V can also be used to derive a minimum rate of hydrogen atom addition to the alkylated sites in tetralin. In these measurements we give the yields of *m*-xylene. This is formed from the displacement of the methyl group from mesitylene by the hydrogen atom. In the present environment styrene can only be formed from the sequence of reactions

$$\text{H} + \text{tetralin} \rightarrow \text{4-phenylbutyl radical} \rightarrow \text{ethylene} + \text{2-phenylethyl} \rightarrow \text{styrene}$$

Thus the ratio of the yields of *m*-xylene to styrene divided by the ratio of mesitylene to tetralin is equal to the ratio of rate constants to the addition of hydrogen to the methyl site in mesitylene to the alkylated sites in tetralin if the phenylethyl radical does not also decompose to form ethylene and a phenyl radical. On this basis we find the ratio of rate constants on a per site basis to be a factor 1.2 in favor of mesitylene. It should be noted that we have found on a per site basis the rate constant for methyl displacement from mesitylene is the same as that from toluene.[10] We call this a minimum number because the results of Fahr and co-workers[13] on phenyl addition to ethylene have found indications of reversibility.

Discussion

The experimental results summarized in the previous section are consistent with the mechanism as given in Figure 6 for the main initial processes in tetralin decomposition. All of these are molecular processes, and radicals are not released into the system. Of course as one goes to higher temperatures, other processes, some of which may produce radicals, may occur. Possible mechanisms are summarized in Figure 7. The important factor is the quantitative results summarized in Table V. Here it can be seen that the chain length is on the order of 10, and hydrogen atom is the main chain carrier. As a result one expects that at lower temperatures and with longer reaction time chain length will be very long, and unless scavengers are used in the ratios employed here the results will always be biased toward chain processes. Furthermore 1,2-dihydronaphthalene is the main chain decomposition product. It is thus extremely difficult to prove the presence of a direct 1,2-elimination in tetralin decomposition studies.

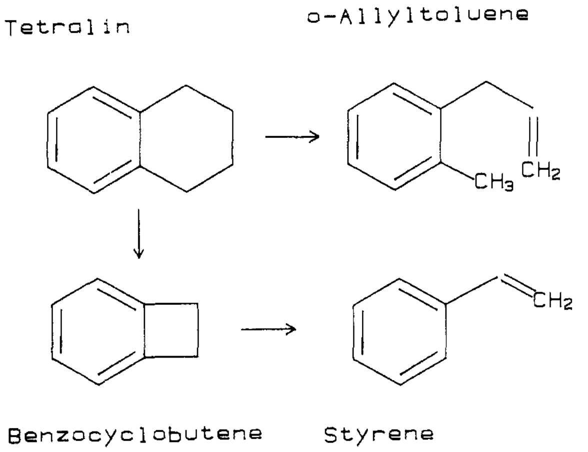

Figure 6. Mechanism for the important initial decomposition processes in tetralin.

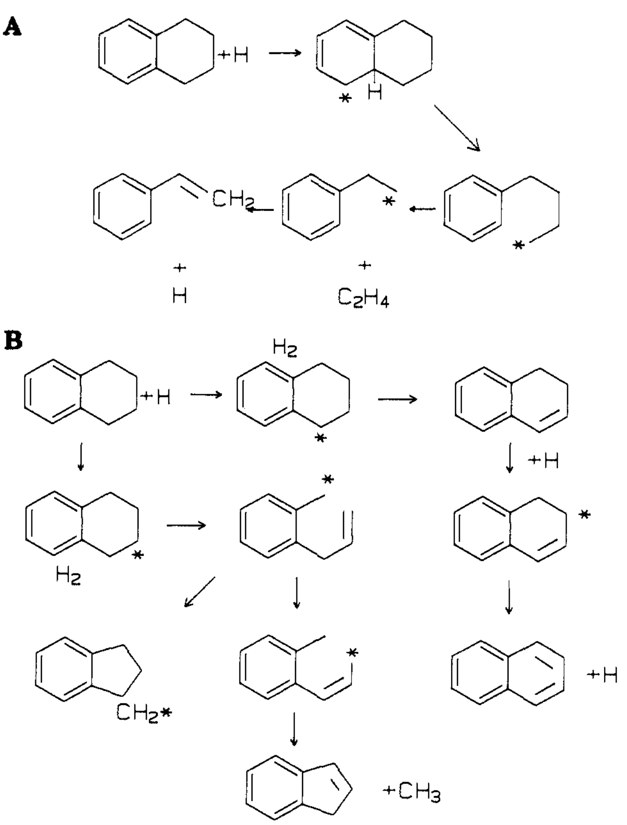

Figure 7. Mechanism for the radical-induced decomposition of tetralin: (A) formation of styrene and (B) formation of 1,2-dihydronaphthalene, naphthalene, indene, and methylindane.

From Figure 1, the expected bond energy for the breaking of the benzylic cabon–carbon bond is 310 kJ/mol. Our measured activation energies for benzocyclobutene and *o*-allyltoluene formation are about 30 kJ/mol higher than the bond energy. These results are inconsistent with a concerted mechanism. Within the framework of a biradical mechanism and assuming that the rate-determining step involves C–C bond cleavage, it is possible to visualize for both processes a transition state that involves not only the elongation of the bond to be broken but also a staggered configuration to remove the radical sites from each other. Such a twist will also bring the β hydrogens into a favorable configuration for internal disproportionation. This is probably the reason for the similarity in activation energy for the two processes. The

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[13] Fahr, A.; Mallard, W. G.; Stein, S. E. *21st Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1986; p 825.

extra increment of energy in excess of the bond energy must have some relation to this twisting motion and presumably have some relation to the height of the barrier for internal rotation. Note that implicit in this mechanism is the conclusion that β bond cleavage from the tetralin diradical has no activation energy. This is readily understood when one realizes that the initially formed diradical is not a true 1,6-diradical but should really be considered a resonance stabilized 1,4-diradical species. Thus the β carbon-carbon bond can be considered to be extremely weak and will not contribute materially to the activation energy. The general situation is similar to that found in isopropenylcyclobutane decomposition.[14]

It is interesting to compare our results with earlier data on cyclohexane decomposition. For the internal disproportionation reaction, that is, the formation of 1-hexene and *o*-allyltoluene from cyclohexane and tetralin, respectively, one sees that there is a degree of parallelism in the difference in the rate expression between the noncyclic and cyclic compounds. The larger activation energy compared to the bond energy is in contrast to the situation for cyclohexene decomposition, a concerted process, where the activation energy is lower. In addition to the activation energy effects there is also a similar decrease in the A-factor for the cyclohexane and tetralin system of about a factor of 3. Presumably this is a reflection of the somewhat more tightened transition state. In the case of cyclopentane decomposition the cyclopropane formation channel involves a β carbon–carbon bond cleavage from the 1,5-diradical. The much larger, 397 kJ/mol activation energy for this process may well contain a contribution from this process.

All of the above is based on the assumption that the expected bond dissociation energy can serve as a marker for concerted versus bond-breaking reactions. That is, if the activation energy for the decomposition process is larger than the bond dissociation energy, then it is proper to consider it a diradical mechanism. This is not without ambiguity, but certainly it is a proper first assumption. On the other hand, if the activation energy is lower than the expected bond dissociation energy, then the bond dissociation process cannot possibly occur, and we are left with the concerted process.

We next consider the conversion of benzocyclobutene to styrene. Proceeding as before we find that under our reaction conditions the breaking of a phenyl–propyl bond requires an activation energy of 431 kJ/mol where we use a heat of formation of phenyl of 339 kJ/mol and 100 kJ/mol for the *n*-propyl radical. If we make the simplest assumption that the strain energy for cyclobutene, 126 kJ/mol, is the same as that for benzocyclobutene, this leads to an activation energy for bond breaking in benzocyclobutene of 305 kJ/mol. This is very close to our experimental determination. Furthermore the A-factor is very similar to other decyclization processes. However, Chapman and Tsou[15] and Trahanovsky and Scribner[16] have carried out extensive mechanistic studies on benzocyclobutene decomposition in flow systems at temperatures close to that of the shock tube studies. Their labeling studies establish in an unambiguous manner that there are major contributions from complex rearrangements involving an *o*-xylxylene intermediate. Thus it would appear that the rate expression that we obtained cannot be identified with any particular process. However, the fact that the activation energy is close to that of the phenyl–carbon bond does suggest some contribution from this bond cleavage channel. This is in accord with the 25% value assigned for this process by Chapman and Tsou.

We now consider the data from the laser-induced decomposition. Of importance is the equality in activation energy for the formation of benzocyclobutene and *o*-allyltoluene. This means that in the direct and the SiF_4-mediated photolysis the ratio of benzocyclobutene to *o*-allyltoluene should be the same as that observed from the truly thermal shock tube experiments. The failure to do so in the direct photolysis indicates that in the course of tetralin photolysis the product *o*-allyltoluene is also being photolytically destroyed. For the SiF_4-induced decomposition, at the lowest energy input, this ratio, where it is assumed that the styrene originates from the benzocyclobutene, is very close to the number that can be derived from our rate expressions. As the temperature is increased this ratio increases in both the laser and shock tube experiments. We have interpreted this in terms of the thermal decomposition of the *o*-allyltoluene. A similar situation occurs in both system with respect to the benzocyclobutene to styrene ratio.

It is apparent that in the SiF_4 sensitized laser experiments initial thermal processes are accessed. Furthermore, chain contributions are probably small. This can be seen from a direct comparison between the laser- and shock-induced decomposition results as summarized in Tables I, IV, and V. Specifically, the results in Table V represent the product distribution to be expected on the basis of a chain mechanism. It is not matched in any way by the distribution from the laser experiments. Instead, the qualitative match is with the maximally inhibited shock tube studies. This is not surprising. The comments we have made on the benefits of the short reaction time holds with even greater force for these laser studies. The heating time could not be more than a few microseconds. There is simply no time for extended chain processes. The real problem with the laser studies is that we are uncertain of the true nature of the physical properties of the system. For mechanistic and especially kinetic purposes the uncertainty in the reaction temperature is particularly serious.

In principle, the fact that tetralin pyrolysis involves a number of sequential and parallel unimolecular decomposition processes whose rate expressions have been determined should permit us to calculate the reaction temperature for the sensitized laser experiments. Unfortunately, our experimental studies led to the same activation energies for benzocyclobutene and *o*-allyltoluene formation from tetralin decomposition. This means that we cannot use the ratio of the yields of the two processes to obtain information on the temperature of the laser experiments, since at any temperature one would obtain the same ratio. The relative yields of styrene to benzocyclobutene leads to another relation, as given above, that relates product concentrations with rate constants, temperature, and heating time. Unfortunately, in the laser experiments only a portion of the sample is illuminated at any given time. Thus after every pulse some of the benzocyclobutene is mixed throughout the photolysis cell, and only a small portion is available for the next heating cycle. We have made calculations for the two extreme cases of no mixing and complete mixing. For the latter we have not been able to fit the data in Figure 1 on the basis of any reasonable assumption. For the nonmixed system the results are compatible with temperatures in the 1200–1300 K range. This must be a minimum number since obviously some mixing must occur during the 1 s between laser pulses. It appears that the temperatures in the laser experiments are close to if not significantly higher than the shock tube experiments at the highest temperatures.

Registry No. Benzocyclobutene, 4026-23-7; styrene, 100-42-5; *o*-allyltoluene, 1587-04-8; indene, 95-13-6; 1,2-dihydronaphthalene, 447-53-0; tetralin, 119-64-2; *o*-methylstyrene, 611-15-4; naphthalene, 91-20-3; methylindene, 29036-25-7; methylindan, 27133-93-3; atomic hydrogen, 12385-13-6.

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(15) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7974.

(16) Trahanovsky, W. S.; Scribner, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7976.