Decomposition, Isomerization, and Ring Expansion in 2-Methylindene: Single-pulse Shock Tube and Modeling Study

Assa Lifshitz,* Carmen Tamburu, Aya Suslensky, and Faina Dubnikova

Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received: October 13, 2003; In Final Form: January 26, 2004

The thermal reactions of 2-methylindene diluted in argon were studied behind reflected shock waves in a 2 in. i.d. pressurized driver single-pulse shock tube over the temperature range 1050−1300 K and overall densities of $\sim 3 \times 10^{-5}$ mol/cm^3. A plethora of products resulting from decompositions, isomerizations, and ring expansion were found in the post shock samples. They were naphthalene as the product of five-membered ring expansion, 1- and 3-methylindene due to isomerizations, and CH_4, C_2H_4, C_2H_6, C_2H_2, benzene, toluene, ethylbenzene, styrene, phenylacetylene, and indene as the result of fragmentation. Very minute yields of some other compounds were also observed. Except for the isomerizations that take place from the reactant as a starting material, the production of all the other products involve free radical reactions. The initiation of the free radical mechanisms in the decomposition of 2-methylindene takes place via ejection of hydrogen atoms from sp^3 carbons and dissociation of the methyl group attached to the ring. The H atoms and the methyl radicals initiate a free radical mechanism by abstraction of hydrogen atoms from sp^3 carbons and by dissociative recombination of H atom and removal of a methyl group from the ring. In addition to these dissociation reactions there are several breakdown processes that involve cleavage of the five-membered ring to produce both stable and unstable products. The ring expansion process that leads to the production of a high yield of naphthalene takes place only from a methylene indene radical intermediate rather than methylindene itself, whereas isomerizations take place from both the radical intermediates and the molecule. The total decomposition of 2-methylindene in terms of a first-order rate constant is given by: $k_{\text{total}} = 10^{13.69}\exp(-59.4 \times 10^3/RT)\ \text{s}^{-1}$. A reaction scheme containing 34 species and 71 elementary reactions was composed and computer simulation was performed over the temperature range 1050−1300 K at 25 K intervals. The agreement between the experimental results and the model prediction for most of the species is satisfactory

Introduction

When a five-membered ring with a methyl group attached to the ring is subjected to high temperatures, in addition to fragmentation, ring expansion and migration of the methyl group from its original site also take place. Moreover, the ring expansion and isomerization products are found to be of very high yield. Experimental results were obtained, modeling and quantum chemical calculations of potential energy surfaces have been performed on molecules such as methylpyrrole,[1−3] dimethylpyrrole,[4] methylindole,[5] methylcyclopentadiene,[6−8] methylindene (quantum chemical calculations)[9] and others. Some of the studies have been published and some are still in the process of data reduction.

Upon ring expansion methylpyrrole produces pyridine, dimethylpyrrole produces two isomers of picoline (methylpyridine), methylindole produces quinoline and isoquinoline, and methylcyclopentadiene produces benzene and higher aromatics. All at high yields.

Quantum chemical calculations on all the compounds mentioned have shown that the ring expansion process does not take place from the molecules but rather from the intermediate radicals that have a methylene group attached to the ring. Isomerizations, on the other hand, take place from both the molecules and the radical intermediates. Except for isomerizations resulting from migrations of the methyl group, no other isomerizations in these molecules were reported. It has been found also that the methyl group shifts play a very important role in the ring expansion process as the energy barriers for the process differ from one isomer to another. Thus, for several isomers isomerization followed by ring expansion is faster than a direct ring expansion.

As far as we are aware, the thermal reactions of 2-methylindene have never been studied in the past. In this investigation we present experimental results and computer modeling of the thermal reactions of 2-methylindene. The rate parameters of the isomerizations and of the ring expansion for the kinetic scheme are based on quantum chemical calculations (at QCISD(T)//B3LYP level of theory). Similarly, the calculated thermodynamic properties of the various radical intermediates are based on the same calculations.

Experimental Procedure and Data Reduction

Shock Tube. The thermal reactions of 2-methylindene were studied behind reflected shock waves in a 2 in. i.d. single pulse shock tube. The driven section, 4 m long, was divided in the middle by a 2 in. ball valve. The driver had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to tune for the best cooling conditions. A 36-L dump tank was connected to the driven section near the diaphragm holder in order to quench transmitted shocks. The driven section was separated from the driver by Mylar polyester film of various thicknesses depending upon the desired shock strength. The tube,

---

* Corresponding author. E-mail: Assa@vms.huji.ac.il

10.1021/jp031160a CCC: $27.50

the gas handling system, the reaction mixture bulbs and the transfer tubes were heated and maintained at 170 °C with an accuracy of ±1 °C.

Reflected shock temperatures were determined from the extent of decomposition of 1,1,1-trifluoroethane which was added in small quantities to the reaction mixtures to serve as an internal standard. Its decomposition to $CH_2{=}CF_2 + HF$ is a first-order unimolecular reaction that under the temperature and pressure of this investigation has a rate constant of $k_{first} = 10^{14.85}\exp(-74.05 \times 10^3/RT)$ s^{-1}, where R is expressed in units of cal/(K mol).[9]

Reflected shock temperatures were calculated from the relation

$$T = -(E/R)/\left[\ln\left\{-\frac{1}{At}\ln(1-\chi)\right\}\right]$$

where t is the reaction dwell time, approximately 2 ms, A and E are the Arrhenius parameters of the standard reaction, and χ is the extent of decomposition defined as

$$\chi = [CH_2{=}CF_2]_t/([CH_2{=}CF_2]_t + [CH_3CF_3]_t)$$

Density ratios were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. Cooling rates were approximately 5 × 10^5 K/s.

Materials and Analysis. Reaction mixtures containing 0.5% of methyl indene diluted in argon were prepared and stored at 1 atm in 12 L glass bulbs. The concentration of the internal standard was 0.1%. The bulbs and the gas handling manifold were pumped down to $\sim 10^{-5}$ Torr. The argon and helium used were of high purity and were used without further purification.

Gas chromatographic analyses of the post shock mixtures provided the product distribution and the temperature (calculated from the ratio $[CH_2{=}CF_2]_t/[CH_3CF_3]_0$). Flame ionization detector (FID) and a temperature-programmed 2-m Porapak N column were used.

The areas under the GC peaks were evaluated using *Chromatograph Station for Windows* software (CWS ver. 1.7) from DataApex Ltd.

Phenyl acetylene and styrene, both products of 2-methylindene decomposition could not be separated on the columns used, so their concentrations were determined with the SIM mode of the GC-MS. The two isomerization products 1-methyl indene and 3-methyl indene could not be separated and could not be determined separately in the GC-MS because of very similar mass spectra. They are presented as one entity.

Evaluation of the Product Concentrations. To avoid errors resulting from irreproducibility of the detector responses, concentrations of reaction products $C_5(\mathrm{pr})_i$ were calculated relative to the concentration of the reactant. Evaluation of the concentrations from the integrated GC peak areas was done using the following relations:

$$C_5(\mathrm{pr})_i = A(\mathrm{pr}_i)_t/S(\mathrm{pr}_i) \times \{C_5(\mathrm{reactant})_0/A(\mathrm{reactant})_0\}$$

$$C_5(\mathrm{reactant})_0 = \{p_1 \times \%(\mathrm{reactant}) \times (\rho_5/\rho_1)/100RT_1\}$$

$$A(\mathrm{reactant})_0 = A(\mathrm{reactant})_t + \frac{1}{n}\Sigma[n(\mathrm{pr}_i) \times A(\mathrm{pr}_i)/S(\mathrm{pr}_i)]$$

where $C_5(\mathrm{reactant})_0$ is the concentration of the reactant behind the reflected shock prior to decomposition, $A(\mathrm{reactant})_0$ is its calculated GC peak area prior to decomposition, and n is the number of its carbon atoms. $A(\mathrm{pr}_i)_t$ is the peak area of a product i in the shocked sample, $S(\mathrm{pr}_i)$ is its sensitivity relative to reactant, and $n(\mathrm{pr}_i)$ is the number of its carbon atoms. ρ_5/ρ_1 is the compression ratio behind the reflected shock wave, and T_1 is the temperature of the reaction mixture prior to shock heating, i.e., the temperature of the shock tube, 170 °C in the present studies.

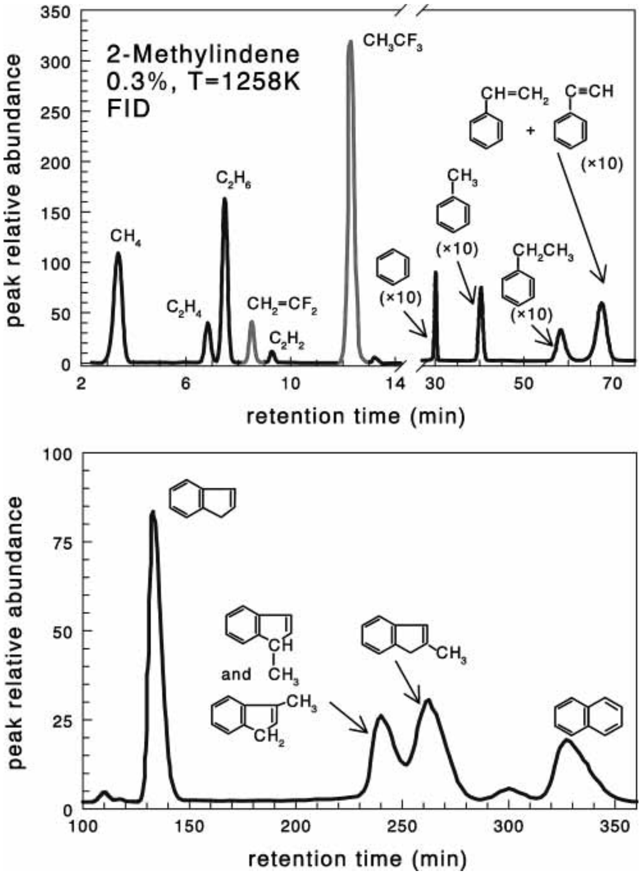


Figure 1. Gas chromatograms of a post-shock mixture of 0.5% 2-methylindene in argon heated to 1258 K, taken on FID.

Results

To determine the distribution of reaction products, some 35 tests were run with mixtures containing 0.5% 2-methylindene and 0.1% 1,1,1-trifluoroethane in argon, covering the temperature range 1050−1300 K. Extents of reaction starting from a few hundredths of one percent were determined. A typical chromatogram of a post shock mixture of 2-methylindene in argon, heated to 1258 K, divided into two parts, is shown in Figure 1. The two peaks CH_3CF_3 and $CH_2{=}CF_2$ in the upper part are those of the chemical thermometer, the ratio of which is used to calculate the temperature behind the reflected shock.

The product distribution is shown graphically in Figure 2. Products of minute quantities were not included. Points for toluene are available only from 1170 K and higher because of unexplained very high scatter. The product distribution is later being used as a basis for comparison between the model prediction and the experimental results.

Figure 3 shows the rate constant for the overall decomposition of 2-methylindene, calculated as a first-order rate constant from the relation

$$k_{total} = -\ln\{[\text{2-methylindene}]_t/[\text{2-methylindene}]_0\}/t$$

The value obtained at the low-temperature end is $k_{total} = 10^{13.69}\exp(-59.4 \times 10^3/RT)$ s^{-1}, where R is expressed in units of cal/

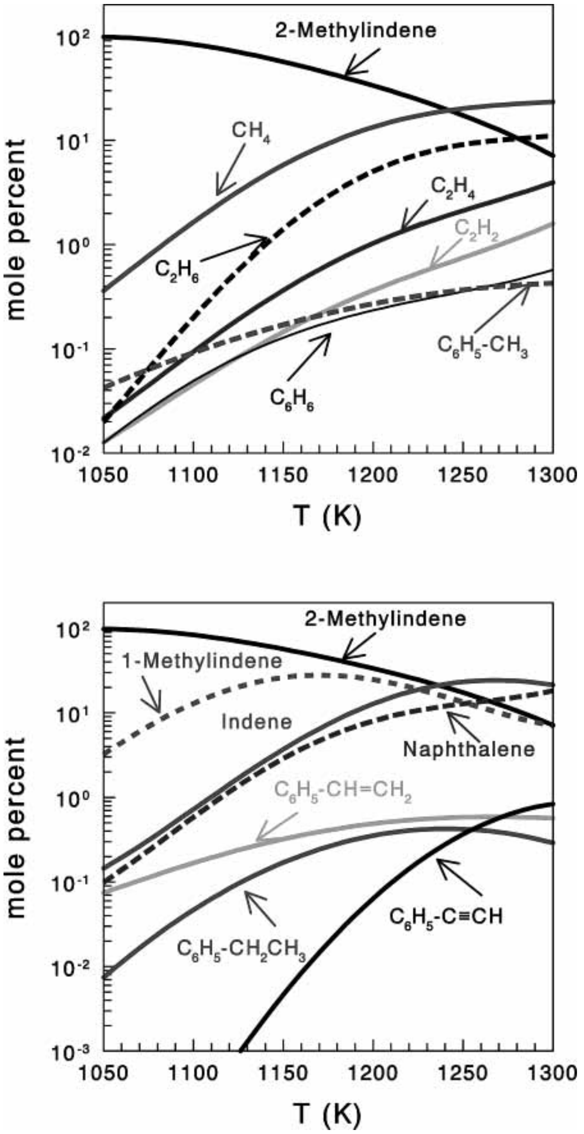


Figure 2. Distribution of reaction products as a function of temperature.

(K mol). Figure 4 shows Arrhenius plots of the first-order production rate of several products, calculated from the relation

$$k_{\text{product}} = \frac{[\text{product}]}{[\text{2-methylindene}]_0 - [\text{2-methylindene}]_t} \times k_{\text{total}}$$

Note that the calculated values correspond to production rates and not to the depletion rate of the reactant due to the production of a given product. Values of *E* obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table 1. The lines are calculated for the lower temperature range of the reaction before further decomposition of the products begins to take place. Since the production of almost all the stable products is associated in one way or another with free radical reactions and are the result of consecutive series of reactions, their parameters do not represent true first-order rate constants. They do provide, however, a convenient way to summarize general rates. Note that the ethane production rate has a high temperature dependence. The reason for this is the relatively high dependence of methyl radical formation as was obtained by the model calculations. Since the only channel for ethane formation is practically methyl radical recombination, its temperature dependence can be as high as twice that of the methyl radical formation.

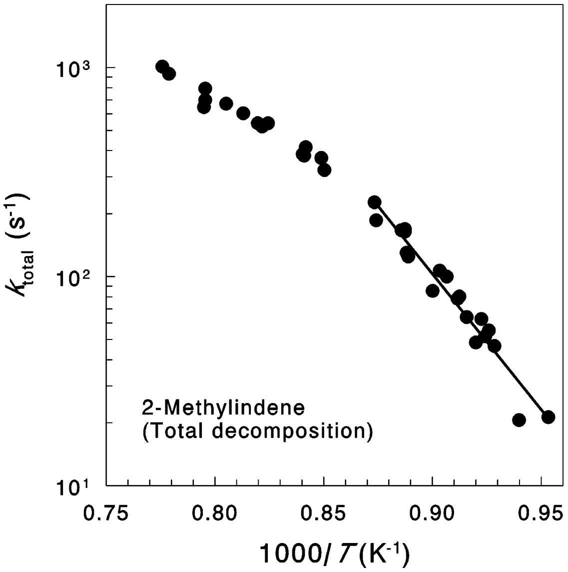


Figure 3. Arrhenius plot of a first-order rate constant for the overall decomposition of 2-methylindene. The rate constant is calculated from the relation $k_{\text{total}} = -\ln\{[\text{2-methylindene}]_t/[\text{2-methylindene}]_0\}/t$. The value obtained for the low-temperature end is $k_{\text{total}} = 10^{13.69} \exp(-59.4 \times 10^3/RT)$ s^{-1}.

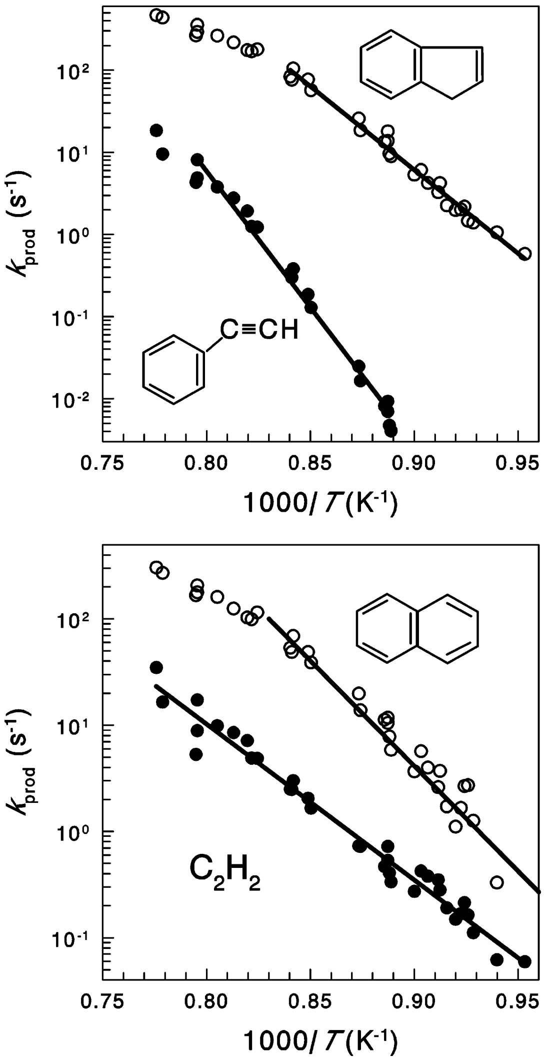


Figure 4. Arrhenius plots for the formation of several reaction products calculated from the relation $k_{\text{product}} = ([\text{product}]_t)/([\text{reactant}]_0 - [\text{reactant}]t) \times k_{\text{total}}$

TABLE 1: First Order Arrhenius Parameters for Production Rates of the Various Reaction Products

product	log (A, s^{-1})	E (kcal/mol)	temp range (K)
2-methylindene (total decomposition)	13.69	59.4	1050−1160
1- and 3-methylindene	12.65	54.5	1050−1150
CH_4	14.63	68.9	1050−1250
C_2H_4	14.12	72.4	1050−1300
C_2H_6	19.53	98.1	1050−1235
C_2H_2	12.74	67.1	1050−1300
C_6H_6	10.18	54.1	1050−1300
$C_6H_5-CH_3$	9.96	52.9	1050−1300
$C_6H_5-CH_2CH_3$	16.29	85.1	1050−1205
$C_6H_5-CH=CH_2$	8.45	42.7	1050−1300
$C_6H_5-C\equiv CH$	27.31	151.8	1060−1250
indene	18.13	88.1	1050−1190
naphthalene	18.4	90.9	1040−1220

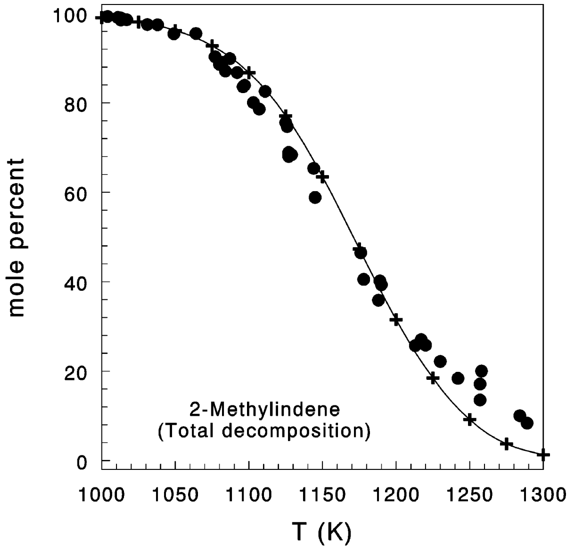


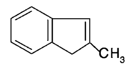
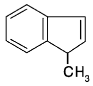
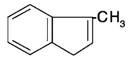
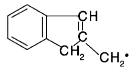
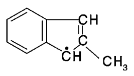
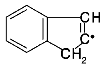
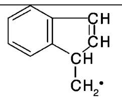
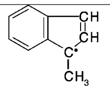
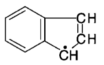
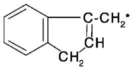
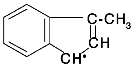
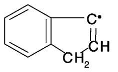
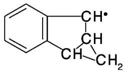
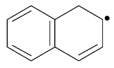
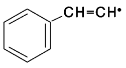
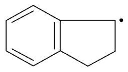
Figure 5. Total decomposition of 2-methylindene. The filled circles are the experimental values and the solid line represents the model prediction. The model calculations were carried out at 25 K intervals and the results are shown as + on the solid line.

Reaction Mechanism. Among the reaction products we find both aromatic and aliphatic hydrocarbons. The main source for the aliphatic components is the methyl group on the cyclopentadiene ring. It can be removed from the ring either by dissociation or by dissociative recombination with hydrogen atoms, where the latter are obtained by the dissociation of the C($_{sp^3}$)-H bonds in the molecule. Three such bonds exist in the methyl group and one in the ring.

The methyl radicals and hydrogen atoms, via a free radical mechanism, produce hydrocarbons, particularly methane, ethane, ethylene, and others in a mechanism that is quite well known and will not be discussed here.

Important reaction channels, without which many of the product yields could not be accounted for, are unimolecular decompositions of the five-membered ring in methylindene. These channels are the unimolecular decompositions to benzyl + propargyl radicals and to styrene + acetylene. They were included in the kinetic scheme. Similar decompositions of the radical intermediates had almost no effect on the distribution of reaction products because of their low concentrations and were thus removed from the kinetic scheme after examining their effect by the sensitivity analysis.

TABLE 2: Glossary and Calculated Thermodynamic Properties of Various Species

Name	Description	$\Delta_f H^\circ$ (298K), kcal/mol	S°(298K), cal/(K mol)
2-Mindene		41.5	87.0
1-Mindene		44.2	86.2
3-Mindene		41.4	86.7
Mindene(R1)•		63.7	86.7
Mindene(R2)•		69.6	86.7
Mindene(R3)•		110.07	85.7
Mindene(R4)•		80.7	89.4
Mindene(R5)•		62.7	86.7
Mindene(R6)•		81.8	78.7
Mindene(R7)•		66.0	86.7
Mindene(R8)•		67.9	86.7
Mindene(R9)•		110.31	85.7
Intermediate(R)•		80.6	84.8
HNaphthalene(R)•		65.9	88.8
Styrene(R)•		93.0	82.2
Indanyl(R)•		62.7	80.9

The ejection of the methyl group from methylindene and abstraction of hydrogen atoms by either hydrogen or methyl produces a large number of radical intermediates that can undergo three main processes. They can isomerize, where the methyl or methylene groups change their position relative to their original site; they can undergo unimolecular decompositions similar to those that take place in the stable molecules (already mentioned before); and those radical intermediates having a methylene group can undergo ring expansion to produce hydronaphthalene radical and then naphthalene. It has been shown by quantum chemical calculations that ring expansion of radical intermediates where the methylene group is

TABLE 3: Reaction Scheme for the Decomposition, Isomerization, and Ring Expansion of 2-Methylindene

No.	reaction	A (mol, s^{-1}, cm^{-3})	E (kcal/mol)	k_f (1150 K)	k_r (1150 K)	ΔS_r (1150 K)	ΔH_r (1150 K)	ref
1	2-mindene → mindene(R1)$^{\bullet}$ + H$^{\bullet}$	1.0×10^{15}	74	8.66	3.39×10^{13}	32.5	77.4	est
2	2-mindene → mindene(R2)$^{\bullet}$ + H$^{\bullet}$ (Rev)	7.0×10^{14}	78	1.05	5.44×10^{13}	32.5	83.3	est
3	2-mindene → mindene(R3)$^{\bullet}$ + $CH_3^{\bullet}$	4.0×10^{16}	93	8.50×10^{-2}	5.97×10^{12}	46.6	100.3	est
4	2-mindene + H$^{\bullet}$ → mindene(R1)$^{\bullet}$ + H_2	1.0×10^{14}	12	5.24×10^{11}	1.17×10^{5}	5.04	−29.2.	est
5	2-mindene + H$^{\bullet}$ → mindene(R2)$^{\bullet}$ + H2	1.0×10^{14}	12	5.24×10^{11}	1.55×10^{6}	5.04	−23.3	est
6	2-mindene + H$^{\bullet}$ → indene + $CH_3^{\bullet}$	8.0×10^{13}	10	1.01×10^{12}	5.29×10^{6}	8.31	−18.2	est
7	2-mindene + $CH_3^{\bullet}$ → mindene(R1)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	2.18×10^{5}	−1.70	−30.3	est
8	2-mindene + $CH_3^{\bullet}$ → mindene(R2)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	2.88×10^{6}	−1.70	−24.4	est
9	2-mindene → 1-mindene	2.86×10^{13}	58.5	219	1.06×10^{3}	−0.810	2.68	9
10	1-mindene → 3-mindene	7.21×10^{13}	38.6	3.33×10^{6}	7.59×10^{5}	0.510	−2.80	9
11	1-mindene → mindene(R4)$^{\bullet}$ + H$^{\bullet}$	3.0×10^{15}	86	0.136	4.79×10^{13}	36.0	91.8	est
12	1-mindene → mindene(R5)$^{\bullet}$ + H$^{\bullet}$	1.0×10^{15}	70	49.9	2.59×10^{13}	33.3	73.8	est
13	1-mindene → mindene(R6)$^{\bullet}$ + $CH_3^{\bullet}$	1.0×10^{16}	65	4.45×10^{3}	1.04×10^{13}	40.4	69.6	est
14	1-mindene + H$^{\bullet}$ → mindene(R4)$^{\bullet}$ + H_2	1.0×10^{14}	13	3.39×10^{11}	6.82×10^{6}	8.55	−14.9	est
15	1-mindene + H$^{\bullet}$ → mindene(R5)$^{\bullet}$ + H_2	1.0×10^{14}	12	5.24×10^{11}	1.56×10^{4}	5.85	−32.9	est
16	1-mindene + H$^{\bullet}$ → indene + $CH_3^{\bullet}$	8.0×10^{13}	10	1.01×10^{12}	1.09×10^{6}	9.12	−20.9	est
17	1-mindene + $CH_3^{\bullet}$ → mindene(R4)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	1.96×10^{7}	1.81	−15.9	est
18	1-mindene + $CH_3^{\bullet}$ → mindene(R5)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	2.90×10^{4}	−0.889	−33.9	est
19	3-mindene → mindene(R7)$^{\bullet}$ + H$^{\bullet}$	1.0×10^{15}	74	8.66	9.16×10^{13}	32.8	80.1	est
20	3-mindene → mindene(R8)$^{\bullet}$ + H$^{\bullet}$ (Rev)	1.0×10^{15}	76	3.61	8.39×10^{13}	32.8	81.9	est
21	3-mindene → mindene(R9)$^{\bullet}$ + $CH_3^{\bullet}$	4.0×10^{16}	93	8.50×10^{2}	5.65×10^{12}	46.9	100.5	est
22	3-mindene + H$^{\bullet}$ → mindene(R7)$^{\bullet}$ + H_2	1.0×10^{14}	12	5.24×10^{11}	3.18×10^{5}	5.34	−26.6	est
23	3-mindene + H$^{\bullet}$ → mindene(R8)$^{\bullet}$ + H_2	1.0×10^{14}	12	5.24×10^{11}	6.98×10^{5}	5.34	−24.8	est
24	3-mindene + H$^{\bullet}$ → indene + $CH_3^{\bullet}$	8.0×10^{13}	10	1.01×10^{12}	4.79×10^{6}	8.61	−18.1	est
25	3-mindene + $CH_3^{\bullet}$ → mindene(R7)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	5.90×10^{5}	−1.40	−27.6	est
26	3-mindene + $CH_3^{\bullet}$ → mindene(R8)$^{\bullet}$ + CH_4	1.0×10^{13}	12	5.24×10^{10}	1.30×10^{6}	−1.40	−25.8	est
27	mindene(R2)$^{\bullet}$ → mindene(R5)$^{\bullet}$	3.0×10^{13}	54.5	1.32×10^{3}	64.5	0	−6.90	9
28	mindene(R4)$^{\bullet}$ → mindene(R5)$^{\bullet}$ (Rev)	3.0×10^{13}	29	9.25×10^{7}	1.37×10^{5}	−2.70	−18	est
29	mindene(R4)$^{\bullet}$ → mindene(R7)$^{\bullet}$ (Rev)	1.50×10^{13}	28	7.17×10^{7}	4.90×10^{5}	−2.70	−14.5	est
30	mindene(R1)$^{\bullet}$ → intermediate(R)$^{\bullet}$	1.28×10^{13}	52.6	1.30×10^{3}	5.82×10^{5}	0.806	14.9	9
31	intermediate(R)$^{\bullet}$ → mindene(R4)$^{\bullet}$ (Rev)	2.46×10^{13}	13.5	6.75×10^{10}	6.62×10^{10}	1.89	2.13	9
32	intermediate(R)$^{\bullet}$ → HNaphthalene(R)$^{\bullet}$	1.98×10^{13}	15.1	2.64×10^{10}	5.67×10^{6}	4	−14.7	9
33	HNaphthalene(R)$^{\bullet}$ → naphthalene + H$^{\bullet}$	1.0×10^{13}	26	1.15×10^{8}	8.75×10^{12}	20.2	22.7	est
34	mindene(R3)$^{\bullet}$ + H$^{\bullet}$ → indene	6.0×10^{13}	0	6.0×10^{13}	4.49×10^{-6}	−38.3	−118.5	est
35	mindene(R6)$^{\bullet}$ + H$^{\bullet}$ → indene	6.0×10^{13}	0	6.0×10^{13}	2.77×10^{-2}	−31.3	−90.5	est
36	mindene(R9)$^{\bullet}$ + H$^{\bullet}$ → indene	6.0×10^{13}	0	6.0×10^{13}	4.30×10^{-6}	−38.3	−118.6	est
37	indene + H$^{\bullet}$ → indanyl(R)$^{\bullet}$	1.0×10^{14}	3	2.69×10^{13}	5.17×10^{7}	−28.6	−36.8	13
38	indanyl(R)$^{\bullet}$ → benzyl$^{\bullet}$ + C_2H_2	3.0×10^{14}	46	5.44×10^{5}	2.92×10^{8}	48.9	44.5	13
39	indanyl(R)$^{\bullet}$ → $C_3H_3^{\bullet}$ + benzene	2.0×10^{14}	49	9.76×10^{4}	3.87×10^{7}	46.3	40.7	13
40	indanyl(R)$^{\bullet}$ → phenylacetylene + $CH_3^{\bullet}$	4.0×10^{14}	48	3.02×10^{5}	2.13×10^{9}	46.0	47.0	13
41	2-mindene → benzyl$^{\bullet}$ + $C_3H_3^{\bullet}$	5.0×10^{15}	83	0.844	9.0×10^{9}	55.8	90.7	est
42	1-mindene → benzyl$^{\bullet}$ + $C_3H_3^{\bullet}$	5.0×10^{15}	83	0.844	1.85×10^{9}	56.6	88.1	est
43	3-mindene → benzyl$^{\bullet}$ + $C_3H_3^{\bullet}$	5.0×10^{15}	83	0.844	8.15×10^{9}	56.1	90.9	est
44	2-mindene → styrene + C_2H_2	2.0×10^{14}	75	1.12	2.26×10^{3}	48.4	46.9	est
45	1-mindene → styrene + C_2H_2	2.0×10^{14}	75	1.12	465	49.2	44.2	est
46	3-mindene → styrene + C_2H_2	2.0×10^{14}	75	1.12	2.05×10^{3}	48.7	47.0	est
47	mindene(R1)$^{\bullet}$ → styrene(R)$^{\bullet}$ + C_2H_2	2.0×10^{14}	103.6	4.11×10^{-6}	3.08×10^{4}	50.1	83.4	est
48	mindene(R2)$^{\bullet}$ → styrene(R)$^{\bullet}$ + C_2H_2	2.0×10^{14}	97.7	5.43×10^{-5}	3.08×10^{4}	50.1	77.5	est
49	mindene(R6)$^{\bullet}$ → styrene(R)$^{\bullet}$ + C_2H_2	2.0×10^{14}	85.5	1.13×10^{-2}	3.07	70.8	68.1	est
50	mindene(R8)$^{\bullet}$ → styrene(R)$^{\bullet}$ + C_2H_2	2.0×10^{14}	99.3	2.70×10^{-5}	3.08×10^{4}	50.1	79.1	est
51	ethylbenzene → benzyl$^{\bullet}$ + $CH_3^{\bullet}$ (Rev)	2.0×10^{16}	73.1	257	1.50×10^{13}	41.5	78.2	14(mod)
52	ethylbenzene + H$^{\bullet}$ → benzene + $C_2H_5^{\bullet}$	5.78×10^{13}	8	1.74×10^{12}	6.64×10^{7}	6.89	−15.3	est
53	toluene → benzyl$^{\bullet}$ + H$^{\bullet}$ (Rev)	1.60×10^{15}	86.9	4.99×10^{-2}	1.40×10^{14}	33.8	93.9	11
54	toluene → phenyl$^{\bullet}$ + $CH_3^{\bullet}$ (Rev)	2.0×10^{16}	96	1.14×10^{-2}	1.84×10^{13}	42.3	102.5	est
55	toluene + H$^{\bullet}$ → benzene + $CH_3^{\bullet}$	5.78×10^{13}	8	1.74×10^{12}	1.84×10^{9}	3.96	−11.1	15
56	benzene → phenyl$^{\bullet}$ + H$^{\bullet}$ (Rev)	6.0×10^{15}	106	4.31×10^{-5}	6.59×10^{13}	38.4	113.6	16
57	ethylbenzene → benzene + C_2H_4	1.15×10^{9}	51.7	0.172	44.4	31.6	22.8	17
58	styrene → benzene + C_2H_2	1.58×10^{11}	58.4	1.24	9.10×10^{5}	29.4	38.5	14
59	styrene → phenylacetylene + H_2	$7.95 \times 10^{12}T^{0.44}$	88.8	2.36×10^{-3}	3.45×10^{3}	28.8	39.4	est
60	styrene(R)$^{\bullet}$ → phenylacetylene + H$^{\bullet}$	1.0×10^{13}	35	2.23×10^{6}	3.94×10^{12}	22.1	32.2	est
61	styrene(R)$^{\bullet}$ + H$^{\bullet}$ → styrene	2.0×10^{14}	0	2.0×10^{14}	1.38×10^{-5}	−34.1	−113.9	est
62	$C_3H_3^{\bullet}$ + $C_3H_3^{\bullet}$ → phenyl$^{\bullet}$ + H$^{\bullet}$	2.0×10^{12}	3	5.38×10^{11}	1.59×10^{10}	−22.1	−33.4	18
63	$C_3H_3^{\bullet}$ + $C_3H_3^{\bullet}$ → benzene	3.0×10^{12}	0	3.0×10^{12}	5.81×10^{-8}	−60.4	−147.1	19
64	CH_4 + H$^{\bullet}$ → $CH_3^{\bullet}$ + H_2	1.44×10^{14}	12.3	6.62×10^{11}	3.56×10^{10}	6.74	1.07	11
65	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → C_2H_6	$1.01 \times 10^{15}T^{-0.64}$	0	1.11×10^{13}	0.462	−40.4	−90.7	20
66	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → $C_2H_5^{\bullet}$ + H$^{\bullet}$	3.01×10^{13}	13.5	8.19×10^{10}	1.42×10^{14}	−4.80	11.5	21
67	$CH_3^{\bullet}$ + $CH_3^{\bullet}$ → C_2H_4 + H_2	1.0×10^{16}	32	8.30×10^{9}	5.59	−7.55	−57.0	22
68	$C_2H_5^{\bullet}$ → C_2H_4 + H$^{\bullet}$	$4.80 \times 10^{9}T^{1.19}$	37.2	1.80×10^{6}	1.22×10^{13}	24.7	38.2	23
69	C_2H_6 + H$^{\bullet}$ → $C_2H_5^{\bullet}$ + H_2	$554.T^{3.50}$	5.17	2.98×10^{12}	7.12×10^{9}	8.18	−4.39	23
70	C_2H_6 + $CH_3^{\bullet}$ → $C_2H_5^{\bullet}$ + CH_4	$0.548\ T^{4.0}$	8.29	2.55×10^{10}	1.13×10^{9}	1.44	−5.47	23
71	$C_2H_5^{\bullet}$ + $CH_3^{\bullet}$ → CH_4 + C_2H_4	$1.95 \times 10^{13}T^{-0.50}$	0	5.75×10^{11}	4.15	−9.49	−69.5	23

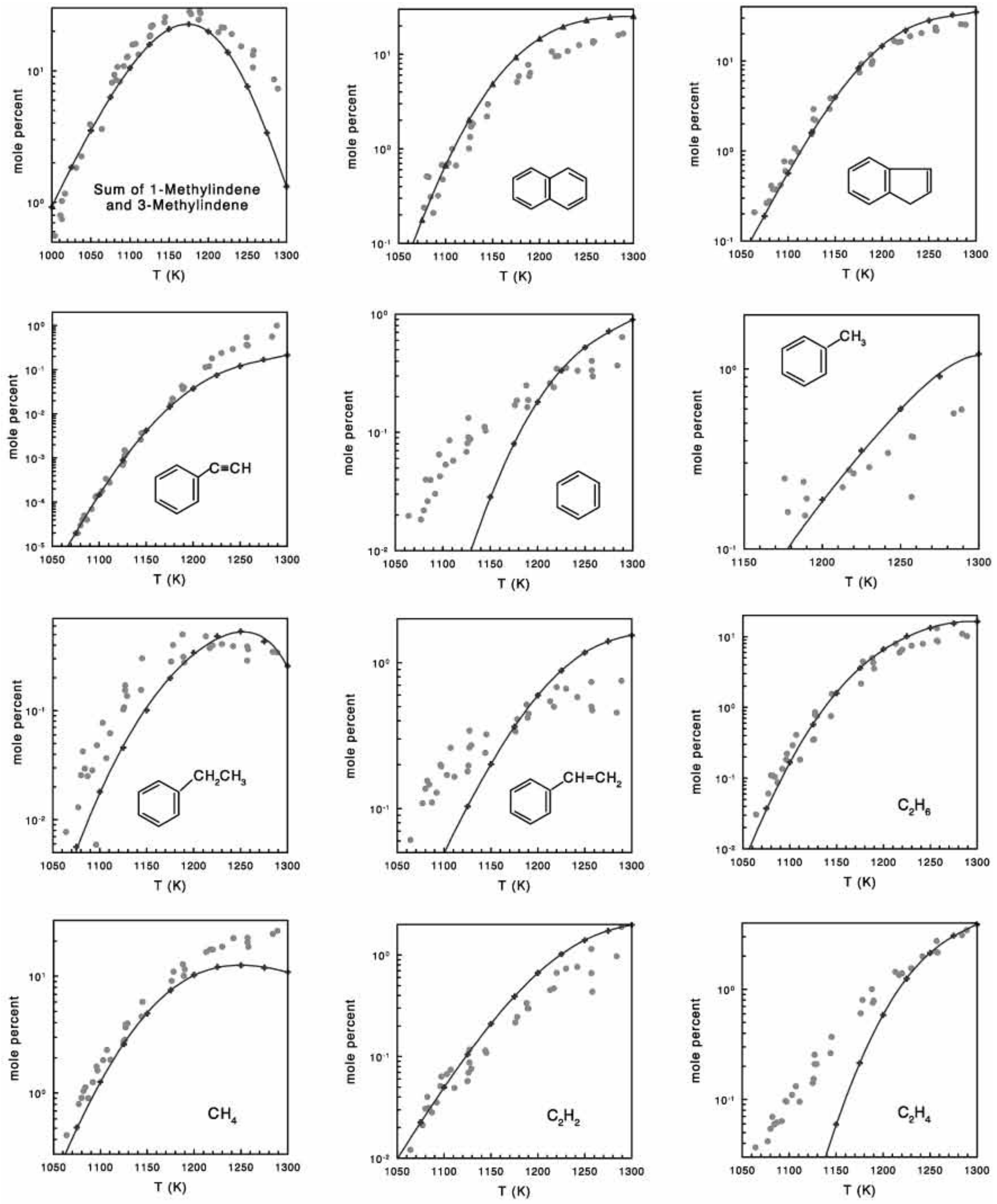


Figure 6. Experimental yields of twelve reaction products plotted against the temperature. The filled circles are the experimental yields and the solid line is the best fit to the calculated yields carried out at 25 K intervals and are shown as + on the solid line.

bound to an sp^2 carbon is rather slow and the migration of the methylene group to an sp^3 carbon followed by ring expansion is faster. The kinetic scheme thus contains ring expansion only from mindene(R4)$^•$ and not from both mindene(R1)$^•$ and mindene(R7)$^•$. Note that the ring expansion from mindene(R4)$^•$ goes via a stable intermediate having a three-membered ring fused to the cyclopentadiene ring (see glossary in Table 2).

Thermochemistry of the Radical Intermediates. Table 2 provides a glossary and calculated thermodynamic properties of the radical intermediates that are formed by the loss of a hydrogen atom or a methyl group from stable methylindene isomers and some additional species. The values were obtained by quantum chemical calculations at the QCISD(T)//B3LYP level of theory, with Dunning correlation consistent polarized valence double ζ (cc-pVDZ) basis set. The values of the heats of formation of the radical intermediates are based on the heat of formation of 2-methylindene taken as 41.7 kcal/mol at 298 K. Any uncertainty in this value is carried over to the other species in the table. Note that the radical mindene(R3)$^•$ obtained by removal of a methyl group from an sp^2 carbon is considerably less stable than all the other radicals.

Computer Modeling. *Reaction Scheme.* To model the observed product distribution we have constructed a reaction scheme that is shown in Table 3. The scheme contains 34 species and 71 elementary reactions. The symbol (Rev) at the end of a listed step in the scheme indicates that after a reaction time of 2 ms (or earlier), the reaction proceeds in the reverse direction. The rate constants listed in the table are given as $k = A \exp(-E/RT)$ or $k = A' \times T^n \exp(-E/RT)$, when the rate constants taken from the database fit a wide temperature range. Units are

TABLE 4: Sensitivity Analysis: Percent Change in the Yield of a Component *i* Due to an Increase in the Rate Constant of Reaction *j* by a Factor of 3, at 1100/1250 K

No.	reaction	1-mindene	3-mindene	indene	naphthalene	ethylbenzene	styrene
1	2-mindene $\rightarrow$ mindene(R1)$^\bullet$ + H$^\bullet$	− / −30	− / −30	50/19	41/18	− / −15	
4	2-mindene + H$^\bullet$ $\rightarrow$ mindene(R1)$^\bullet$ + H_2			−21/−			
5	2-mindene + H$^\bullet$ $\rightarrow$ mindene(R2)$^\bullet$ + H2			−22/−			
6	2-mindene + H$^\bullet$ $\rightarrow$ indene + $CH_3^\bullet$			39/−			
7	2-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R1)$^\bullet$ + CH_4	− / −20	− / −20		16/16	−17 / −14	
8	2-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R2)$^\bullet$ + CH_4	− / −19	− / −19		13/16	−17 / −14	
9	2-mindene $\rightarrow$ 1-mindene	139/−	140/−	50/−	60/−	16/−	
12	1-mindene $\rightarrow$ mindene(R5)$^\bullet$ + H$^\bullet$	− / −29	− / −29	−/18	−/16	− / −12	
13	1-mindene $\rightarrow$ mindene(R6)$^\bullet$ + $CH_3^\bullet$			11/−	13/−		
19	3-mindene $\rightarrow$ mindene(R7)$^\bullet$ + H$^\bullet$	− / −24	− / −24	−/15	−/13	− / −10	
27	mindene(R2)$^\bullet$ $\rightarrow$ mindene(R5)$^\bullet$			26/−	42/−		
30	mindene(R1)$^\bullet$ $\rightarrow$ intermediate(R)$^\bullet$			38/−	63/−		
35	mindene(R6)$^\bullet$ + H$^\bullet$ $\rightarrow$ indene	−/−10	−/−11	18/12		−/19	
38	indanyl(R)(R)$^\bullet$ $\rightarrow$ benzyl$^\bullet$ + C_2H_2					−/29	
41	2-mindene $\rightarrow$ benzyl$^\bullet$ + $C_3H_3^\bullet$					187/109	
43	3-mindene $\rightarrow$ benzyl$^\bullet$ + $C_3H_3^\bullet$					−/42	
44	2-mindene $\rightarrow$ styrene + C_2H_2						188/135
51	ethylbenzene $\rightarrow$ benzyl$^\bullet$ + $CH_3^\bullet$ (Rev)					39/−	
53	Toluene $\rightarrow$ benzyl$^\bullet$ + H$^\bullet$ (Rev)				0	−24 / −47	
65	$CH_3^\bullet$ + $CH_3^\bullet$ $\rightarrow$ C_2H_6			−3	− / −16	− / −17	

No.	reactions	phenylacetylene	toluene	benzene	C_2H_6	C_2H_4	C_2H_2	CH_4
1	2-mindene $\rightarrow$ mindene(R1)$^\bullet$ + H$^\bullet$	138/75	30/23		20/−	43/34		
4	2-mindene + H$^\bullet$ $\rightarrow$ mindene(R1)$^\bullet$ + H_2	−39/−	−17/−			−15/−		
5	2-mindene + H$^\bullet$ $\rightarrow$ mindene(R2)$^\bullet$ + H2	−40/−	−18/−					
6	2-mindene + H$^\bullet$ $\rightarrow$ indene + $CH_3^\bullet$		−37/−		20/−			
7	2-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R1)$^\bullet$ + CH_4	14/17	23/−		−50/−16	−50 / −14		34/40
8	2-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R2)$^\bullet$ + CH_4	−/13	18/−		−51/−16	−52 / −15		33/41
9	2-mindene $\rightarrow$ 1-mindene	65/−23	−15/−28	0/−18	157/11	198/−	− / −14	61/−
12	1-mindene $\rightarrow$ mindene(R5)$^\bullet$ + H$^\bullet$	19/68	−/25			−/30		
13	1-mindene $\rightarrow$ mindene(R6)$^\bullet$ + $CH_3^\bullet$	11/−			35/−	44/−		19/−
19	3-mindene $\rightarrow$ mindene(R7)$^\bullet$ + H$^\bullet$	14/53	−/20			−/24		
25	3-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R7)$^\bullet$ + CH_4	11/10						
26	3-mindene + $CH_3^\bullet$ $\rightarrow$ mindene(R8)$^\bullet$ + CH_4	−/−13				− / −13		−/15
27	mindene(R2)$^\bullet$ $\rightarrow$ mindene(R5)$^\bullet$	60/−	20/−			23/−		
30	mindene(R1)$^\bullet$ $\rightarrow$ intermediate(R)$^\bullet$	93/−	28/−		14/−	34/−		
35	mindene(R6)$^\bullet$ + H$^\bullet$ $\rightarrow$ indene	−14/−47	−18/−41			−11/−28		
38	indanyl(R)$^\bullet$ $\rightarrow$ benzyl$^\bullet$ + C_2H_2		−/16				−/25	
39	indanyl(R)$^\bullet$ $\rightarrow$ $C_3H_3^\bullet$ + benzene			−/19				
40	indanyl(R)$^\bullet$ $\rightarrow$ phenylacetylene + $CH_3^\bullet$	194/180						
41	2-mindene $\rightarrow$ benzyl$^\bullet$ + $C_3H_3^\bullet$		197/128	529/135				
43	3-mindene $\rightarrow$ benzyl$^\bullet$ + $C_3H_3^\bullet$		−/35	13/42				
44	2-mindene $\rightarrow$ styrene + C_2H_2						187/116	
46	3-mindene $\rightarrow$ styrene + C_2H_2						−/39	
51	ethylbenzene $\rightarrow$ benzyl$^\bullet$ + $CH_3^\bullet$ (Rev)		−46/−					
53	toluene $\rightarrow$ benzyl$^\bullet$ + H$^\bullet$ (Rev)		123/63					
62	$C_3H_3^\bullet$ + $C_3H_3^\bullet$ $\rightarrow$ phenyl$^\bullet$ + H$^\bullet$		−/16	−/−16				
63	$C_3H_3^\bullet$ + $C_3H_3^\bullet$ $\rightarrow$ benzene			129/17				
65	$CH_3^\bullet$ + $CH_3^\bullet$ $\rightarrow$ C_2H_6	− / −32			102/32	26 / −12		−17/−32
66	$CH_3^\bullet$ + $CH_3^\bullet$ $\rightarrow$ $C_2H_5^\bullet$ + H$^\bullet$					89/17		
69	C_2H_6 + H$^\bullet$ $\rightarrow$ $C_2H_5^\bullet$ + H_2					76/94		
70	C_2H_6 + $CH_3^\bullet$ $\rightarrow$ $C_2H_5^\bullet$ + CH_4					20/50		

cm^3, mol^{-1}, s^{-1}, and kcal/mol. The Arrhenius parameters for the reactions in the scheme are either estimated or taken from various literature sources. These sources are specific articles relevant to the present system and databases, mainly the NIST-Kinetic Standard Reference Data Base #17. The parameters for the reactions that were taken from the NIST-Kinetics Data Base are, in many cases, best fits to a large number of entries. The rate parameters for the ring expansion of mindene(R4)$^\bullet$ and of the methyl/methylene group shifts are based on the quantum chemical calculations. The thermodynamic properties of the species in the scheme were also taken from specific articles and various literature sources. Some were estimated using NIST-Standard Reference Data Base #25 (Structure and Properties program (SP)). As has been mentioned before, the thermodynamic properties of the radical intermediates and of several other species (Table 2) were calculated using quantum chemical methods at the QCISD(T)// B3LYP level of theory.

Figure 5 shows the overall disappearance of the reactant 2-methylindene, and Figure 6 shows experimental and calculated yields of twelve products found in the post-shock mixtures. The symbols (●) in the figures are the experimental yields in mole percent and the lines are best fits to the calculated points using the scheme shown in Table 3. The calculations were done at 25 K intervals in the temperature range 1050−1300 K and are shown as (+) on the lines. The agreement between the model prediction and the experimental results is reasonable for most of the products. The model underestimates the yield of benzene, styrene, and ethylene at the low-temperature end. Using the sensitivity analysis we tried to change rate parameters within the limits of their uncertainties but were unable to improve the overall agreement between the calculations and the experimental results.

Sensitivity Analysis. Table 4 shows the sensitivity of the system to variation of specific reactions in the kinetic scheme,

TABLE 5: Sensitivity Analysis: Percent Change in the Yield of a Component *i* Due to an Increase in the Value of $\Delta_fH°$ of a Species *j* by 5 kcal/mol, at 1100/1250 K

species	1-mindene	3-mindene	indene	naphthalene	ethyl-benzene	styrene	phenyl-acetylene	toluene	benzene	C_2H_6	C_2H_4	C_2H_2	CH_4
2-mindene			22/−	11/−			46/11	16/−		12/18	24/19		
1-mindene	−86/−79	28/56	−27/−11	−33/−	−34/−	−/22	−27/18	28/46		−78/−24	−80/−18	−/21	−53/−
3-mindene	173/13	−72/−84	46/−	50/−	18/−	−2/−13	48/ −	−23/−22	−/−15	184/15	222/11	−/−12	69/−
mindene(R1)$^\bullet$	−/20	−/21	−33/−12	−16/−11	−/11		−55/−33	−29/−10		−10/−	−25/−17		
mindene(R2)$^\bullet$	−/13	−/13	−31/−	−15/−			−52/−22	−28/−		−10/−	−24/−11		
mindene(R3)$^\bullet$													
mindene(R4)$^\bullet$													
mindene(R5)$^\bullet$													
mindene(R6)$^\bullet$	−/61	−/61	−18/−	−22/19	−31/−27	−/28	−14/153	27/126	−/68	−72/−45	−71/−	−/46	−45/−10
mindene(R7)$^\bullet$													
mindene(R8)$^\bullet$													
mindene(R9)$^\bullet$													
HNaphthalene(R)$^\bullet$													
intermediate(R)$^\bullet$													
indanyl(R)$^\bullet$					−/−14		−88/−81					−/−12	
styrene(R)$^\bullet$													

calculated at 1100 and 1250 K, respectively. The table gives the percent change in the yield of a particular product for a factor of 3 increase in the rate constant of a particular reaction. The calculations correspond to a dwell time of 2 ms. Reactions that show an effect of less than 10%, both at 1100 K and at 1200 K, are not included in the table.

We have run also sensitivity analyses with respect to variations (or rather uncertainties) in the $\Delta_fH°$ of species whose thermodynamic properties were estimated or calculated. Note that incorrect values of the thermodynamic properties result in erroneous values for the rate constants of the back reactions for a given value of the forward rate constant. The sensitivity spectrum calculated at 1100 and 1250 K is shown in Table 5. It gives the effect of an increase of 5 kcal/mol in the $\Delta_fH°$ of the species on the product yields. As can be seen, there is a significant effect on some of the products. Special attention should be paid to the effect caused by variation in the $\Delta_fH°$ of the calculated radical intermediates.

It should be mentioned that whereas ring expansion (production of naphthalene) depends on the concentrations of the radical intermediates (as expansion does not take place from the molecules), the contribution of the radical reactions to isomerization is practically negligible since the molecules do interisomerize. Since their concentrations are much higher than those of the radicals, their contribution to the isomerization process is significantly greater.

Conclusions

Methylindene undergoes decompositions, isomerizations (methyl group shifts), and ring expansion to hydronaphthalene when elevated to high temperatures. Both aliphatic and new aromatic compounds are formed in the process.

Ring expansion takes place *only* from radical intermediates that have a methylene group connected to the five-membered ring. Ring expansion from mindene(R4)$^\bullet$ (see Table 2), where the methylene group is connected, an sp^3 carbon is much faster than ring expansion from mindene(R1)$^\bullet$ and mindene(R7)$^\bullet$, in which the methylene group is connected to an sp^2 carbon.

The rate constant of the isomerization 1-methylindene → 3-methylindene is much higher than the rate constants for both 1-methylindene → 2-methylindene and 2-methylindene → 3-methylindene isomerizations as 1-methylindene → 3-methylindene isomerization involves H-atom shifts (double 1,2-shifts) only, whereas the other two involve methyl group migration with considerably higher barriers.

A model containing 71 elementary steps and 34 species, both stable and unstable, was constructed. The model prediction is satisfactory except for the yields of benzene, styrene, and ethylene at the low-temperature end of the range where the yields are underestimated.

Acknowledgment. This work was supported by a grant from the Israel Science Foundation (ISF) #34/01.

References and Notes

(1) Lifshitz, A.; Shweky, I.; Tamburu, C. *J. Phys. Chem.* **1993**, *97*, 4442.

(2) Doughty, A.; Mackie, J. C.; Bacskay, G. B. *Chem. Phys. Lett.* **1994**, *221*, 267.

(3) Dubnikova, F.; Lifshitz, A. *J. Phys. Chem. A.* **2000**, *104*, 530.

(4) Lifshitz, A.; Suslensky, A.; Tamburu, C. *J. Phys. Chem. A* **2003**, *107*, 4851.

(5) Lifshitz, A.; Suslensky, A.; Tamburu, C., unpublished results (experimental). Dubnikova, F.; Lifshitz, A., unpublished results (quantum chemical calculations).

(6) Dubnikova, F.; Lifshitz, A. *J. Phys. Chem. A* **2002**, *106*, 8173.

(7) Ikeda, E.; Tranter, R. S.; Kiefer, R. D.; Kern, R. D.; Singh, H. J.; Zhang, Q. *Proc. Combust. Inst.* **2000**, *28*, 1725.

(8) Lifshitz, A.; Suslensky, A.; Tamburu, C., unpublished results (experimental).

(9) Dubnikova, F.; Lifshitz, A. *Isr. J. Chem*., in press.

(10) Tsang, W.; Lifshitz, A. *Int. J. Chem. Kinet*. **1998**, *30*, 621.

(11) Westly, F.; Herron, J. T.; Cvetanovic, R. J.; Hampson, R. F.; Mallard W. G. *NIST-Chemical Kinetics Standard Reference Database 17*, Version 5.0, National Institute of Standards and Technology: Washington, DC.

(12) Stein S. E.; Rukkers J. M.; Brown R. L. *NIST-Standard Reference Database 25*. National Institute of Standards and Technology: Washington, DC.

(13) Laskin, A.; Lifshitz, A. Thermal Decomposition of indene. Experimental results and kinetic modeling. In *Proceedings of the 27th Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1998; pp 313−320.

(14) Muller-Markgraf, W.; Troe, J. *J. Phys. Chem.* **1988**, *92*, 4914.

(15) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, Th.; Kerr, J. A.; Murrells, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1994**, *23*, 847−1033.

(16) Hsu, D. S. Y.; Lin, C. Y.; Lin, M. C. *Proc. Combust. Inst*. **1985**, *20*, 623.

(17) Clark, W. D.; Price, S. J. *Can. J. Chem*. **1970**, *48*, 1059.

(18) Burcat, A.; Dvinyaninov, M. *Int. J. Chem. Kinet*. **1997**, *29*, 505−514.

(19) Wu, C. H.; Kern, R. D. *J. Phys. Chem*. **1987**, *91*, 6291.

(20) Tsang, W. *Combust. Flame* **1989**, *78*, 71−86.

(21) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411−429.

(22) Warnatz, J. Rate coefficients in the C/H/O system. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.

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

(24) Brand, U.; Hippler, H.; Lindemann, L.; Troe, J. *J. Phys. Chem.* **1990**, *94*, 6305.

(25) Muller, C.; Warth, V.; Jacquemard, E.; Scacchi, G.; Come, G. M. A FORTRAN computer code package for the evaluation of thermochemical data of molecules, free radicals, and reactions in the gas phase and A. S. T. M. CHETAH safety criteria., 1996.

(26) Burcat, A. *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion*, Technion Aerospace Engineering (TAE), Report # 867, January 2001.