# Thermal Isomerization of Azulene. Single-Pulse Shock Tube Investigation

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Abstract. The thermal isomerization of azulene was studied behind reflected shocks in a pressurized driver single-pulse shock tube. The temperature range covered was 1050–1400 K at overall densities of ~2.5 × 10<sup>-5</sup> mol/cm<sup>3</sup>. The main reaction of azulene under these conditions is a unimolecular isomerization to naphthalene, but it also isomerizes, although at a much lower rate, to another isomer. The suggested "tetracyclic triene" intermediate structure for the azulene–naphthalene isomerization can lead also to transition states that can describe isomerizations to 1-methylene-1H-indene and 1,2,3-metheno-1H-indene,2,3-dihydro. Small quantities of  $C_2H_2$ ,  $C_4H_2$ ,  $C_6H_6$ , and  $C_6H_5$ –C=CH were also found in the post-shock samples, particularly at high temperatures. The Arrhenius parameters of the two high pressure limit rate constants for the isomerization processes are:

azulene  $\rightarrow$  naphthalene,  $k_1 = 10^{12.93} \exp(-62.8 \times 10^3/RT) \text{ s}^{-1}$ azulene  $\rightarrow$  second isomer,  $k_2 = 10^{12.42} \exp(-69.5 \times 10^3/RT) \text{ s}^{-1}$ 

A discussion of the mechanism for these isomerization processes is presented.

# INTRODUCTION

The study of the thermal isomerization of azulene dates back to the early work of Heilbronner and Wieland,<sup>1</sup> who first reported a thermal isomerization of azulene to naphthalene. Later, Heilbronner<sup>2</sup> reported the first-order limit rate constant for the isomerization over the temperature range 650–700 K, as  $\Delta H^{\#} = 48.8 \pm 0.8$  kcal/mol and  $\Delta S^{\#} = -5.3 \pm 3.6$  eu.

Alder et al.<sup>3</sup> studied the thermolysis of 2-methylazulene in a static system at 440 °C. The NMR analysis of the products showed a nearly 2:1 ratio of  $\beta$ - and  $\alpha$ methylnaphthalene. On the basis of these results, the authors came to the conclusion that the methylazulene– methylnaphthalene isomerization proceeded via a freeradical reaction mechanism. They assumed also a similar behavior in azulene isomerization.

Scott and Agopian<sup>4</sup> studied the scrambling of  $\alpha$  and  $\beta$  carbon atoms in naphthalene at high temperatures using <sup>13</sup>C labeling. A unimolecular pathway involving azulene as an intermediate was suggested for this process.

Brouwer and Troe<sup>5</sup> investigated in detail the kinetics of azulene–naphthalene isomerization at high temperatures. The isomerization was studied in a shock tube by monitoring azulene and naphthalene light absorption in the UV at 272 and 220 nm, respectively. The investigation was performed over the temperature range 1300– 1900 K and overall densities of  $2.0 \times 10^{-6} - 2.0 \times 10^{-4}$ mol/cm<sup>3</sup>. These experiments showed that the thermal isomerization of azulene to naphthalene under high temperature conditions is a clean unimolecular reaction. After correcting for fall-off effects, a high pressure limit rate constant  $k_{\infty} = 10^{12.93} \exp(-62.8 \times 10^3/RT) \text{ s}^{-1}$  was derived. Based on this  $k_{\infty}$ , specific rate constants k(E) for further photoexcitation studies<sup>6</sup> were deduced.

The present investigation was performed in a singlepulse shock tube at a lower temperature range, 1050– 1400 K. Very good agreement with the results of Brouwer and Troe<sup>5</sup> was obtained. The mechanism for the formation of a second isomerization product is discussed.

### **EXPERIMENTAL SECTION**

#### Apparatus

The thermal isomerization of azulene was studied behind reflected shocks in a pressurized driver, 52-mm i.d. heated single-pulse shock tube. The tube and its gas-handling system \*Author to whom correspondence should be addressed.

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were maintained at  $150 \pm 1$  °C. The driven section was 4 m long, and the driver had a variable length up to a maximum of 2.7 m and could be varied in small steps in order to obtain the best cooling conditions. Cooling rates were approximately  $5 \times 10^5$  K/s. A 36-L dump tank was connected to the driven section at a 45° angle near the diaphragm holder in order to prevent reflection of transmitted shocks. The driven section was separated from the driver by a Mylar polyester film of various thickness, depending upon the desired shock strength.

Prior to performing an experiment, the tube and the gashandling system were pumped down to  $\sim 3 \times 10^{-5}$  Torr. After running an experiment, a gas sample was transferred from the tube, through a heated injection system, to a Hewlett-Packard Model 5890A gas chromatograph operating with a flame ionization detector. A detailed description of the apparatus and its mode of operation were given in earlier publications.<sup>7,8</sup>

The reflected shock temperatures were calculated from the extent of decomposition of 1,1,1-trifluoroethane (CF<sub>3</sub>CH<sub>3</sub>  $\rightarrow$  CF<sub>2</sub>CH<sub>2</sub> + HF) which was added in small quantities to the reaction mixture to serve as an internal standard. This decomposition is a first-order unimolecular reaction<sup>9</sup> with a rate constant given by  $k_{1st} = 10^{14.51} \exp(-72.7 \times 10^3/RT) \text{ s}^{-1}$ . The reflected shock temperatures were calculated from the relation:

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

where E is the activation energy of the standard reaction, A is its preexponential factor, t is the reaction dwell time, and  $\chi$  is the extent of decomposition defined as:

$$\chi = [CF_2CH_2]_{\prime} / ([CF_2CH_2]_{\prime} + [CF_3CH_3]_{\prime})$$
(2)

The remaining reflected shock parameters were calculated from the measured incident shock velocities, using the three conservation equations and the ideal gas equation of state. The molar enthalpies of azulene were taken from Stull et al.<sup>10</sup> Reaction dwell time was approximately 2 ms.

#### Materials and Analysis

Reaction mixtures containing 0.3% azulene and 0.05% 1,1,1-trifluoroethane in argon were prepared in 12-L glass bulbs and stored at 700 Torr. Both the bulbs and the line were pumped down to approximately  $10^{-5}$  Torr before preparation of the mixtures. The evacuated bulb was first filled with pure argon to 1 atm, then crystals of azulene at a known weight were injected into the bottom part of the bulb through a special inlet. This part was then frozen with liquid nitrogen and the bulb was pumped down to ~ $10^{-4}$  Torr. After being heated and maintained for several hours at 150 °C the bulb was filled to 700 Torr with a mixture of 0.05% 1,1,1-trifluoro-ethane in argon. Experiments were carried out at least 24 hours after the preparation of the mixtures. It should be mentioned that 0.3% of azulene in the gas-phase mixture corresponds approximately to 5% of its equilibrium vapor pressure at 150 °C.

Azulene, 99.0% pure, obtained from Aldrich Chemical Co., showed only one GC peak. 1,1,1-trifluoroethane, 99.0%

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pure, obtained from P.C.R. Inc., also showed only one GC peak. The argon used was Matheson ultrahigh-purity grade, listed as 99.9995%, and the helium was Matheson pure grade, listed as 99.999%. All materials were used without further purification.

Gas chromatographic analyses of the post-shock mixtures were performed on two columns with flame ionization detectors. The analyses of light hydrocarbons, coming from decomposition processes, were performed on a 2-m Porapak N column, and the products with large numbers of carbon atoms were analyzed on a methyl silicone capillary column. The sensitivities of the products to the FID were determined relative to azulene from standard mixtures. The areas under the GC peaks were integrated with a Spectra Physics Model SP4200 computing integrator and were transferred after each analysis to a PC for data reduction and graphical presentation. Identification of the reaction products was based on their GC retention times, with the aid of their mass spectra determined with a Hewlett-Packard Model 5970 MSD.

# RESULTS

Some 40 experiments with mixtures containing 0.3% azulene and 0.05% 1,1,1-trifluoroethane in argon were run, covering the temperature range 1050–1400 K. Over this temperature range, the main reaction product is naphthalene. A GC-MS analysis showed that the small peak which appears just before the naphthalene peak on the methyl silicone column has a mass spectrum similar to that of azulene and naphthalene. Figure 1 shows a single-ion chromatogram of the parent ion (m/z = 128) and the mass spectum of the small peak.

Details of the experimental conditions and the product distribution in the post-shock mixtures are given in Table 1. The numbers in the column which indicate total decomposition are expressed in terms of loss in the azulene concentration. Figure 2 is a detailed graphical presentation of these results. As can be seen, the extent of decomposition, as compared to the isomerization, is minimal up to very high conversions of azulene. The main decomposition products are  $C_2H_2$ ,  $C_4H_2$ ,  $C_6H_6$ , and  $C_6H_5-C\equiv CH$ .

Figures 3 and 4 show Arrhenius plots of the firstorder rate constants of the isomerization reactions, calculated from the relation:

$$k_{i} = \{[\text{isomers}]_{i,t} / (\Sigma[\text{isomers}]_{t} + (1/10) \\ \times \Sigma N(\text{pr}_{i})C(\text{pr}_{i})_{t})\} \times k_{\text{total}}$$
(3)

where:

$$k_{\text{total}} = -\ln([\text{azulene}]_t / [\text{azulene}]_0)/t$$
 (4)

In these relations  $N(pr_i)$  is the number of carbon atoms in a decomposition product and  $C(pr_i)$ , is its concentration. The Arrhenius line of Brouwer and Troe<sup>5</sup> at higher temperatures is also shown in Fig. 3.





Methyl Silicone Column, T=1300 K

Fig. 1. a. Single-ion chromatogram of shock-heated mixture of 0.3% azulene (1300 K), taken on methyl silicone column. b. Mass spectrum of the second isomeric product.



T₅,K	Dwell time (ms)	$C_5 \times 10^5$ mol/cm <sup>3</sup>	Azulene	Naphtha- lene	Isomer	Decompo- sition
1050	2 30	1 72	00 73	0.27		products
1076	2.30	1.72	00.68	0.27		
1095	2.20	1.70	98.17	1.81	0.02	
1100	2.18	1.07	99.52	0.48	0.02	
1104	2.17	1.95	99.44	0.40		
1117	2.27	1.96	98.95	1.04	0.01	
1132	2.15	1.99	98.61	1.39	0.01	
1150	2.03	2.04	98.41	1.59		
1152	2.08	2.04	96.38	3.58	0.04	
1160	2.02	1.98	97.91	2.06	0.03	
1172	2.10	2.13	94.81	5.12	0.07	
1174	2.03	2.13	95.38	4.54	0.08	
1175	2.13	2.13	95.48	4.45	0.07	
1200	2.02	2.23	93.08	6.79	0.13	
1200	2.00	2.23	92.00	7.85	0.16	
1207	1.97	2.20	94.41	5.47	0.12	
1207	2.04	2.20	91.02	8.84	0.14	
1210	2.00	2.28	91.51	8.36	0.13	
1215	2.15	2.28	89.62	10.15	0.23	
1240	2.04	2.28	88.97	10.84	0.19	
1243	1.98	2.38	81.56	17.96	0.43	0.05
1245	1.96	2.37	87.20	12.62	0.18	
1248	2.01	2.38	83.30	16.19	0.36	0.15
1248	1.95	2.38	79.95	19.48	0.54	0.03
1250	2.10	2.38	79.83	19.44	0.47	0.27
1251	1.96	2.43	79.05	20.28	0.54	0.13
1256	2.03	2.43	78.40	20.90	0.56	0.13
1259	2.00	2.41	84.29	15.39	0.32	
1265	1.98	2.38	75.21	24.04	0.56	0.19
1271	2.02	2.43	69.59	29.23	0.94	0.24
1290	1.94	2.53	63.10	35.37	1.14	0.39
1300	1.92	2.59	74.67	24.36	0.71	0.26
1320	2.01	2.62	56.27	41.96	1.26	0.51
1322	1.86	2.64	45.95	51.31	1.62	1.12
1330	1.96	2.69	41.61	54.17	0.96	3.27
1335	1.88	2.64	40.41	56.52	1.43	1.65
1340	2.00	2.75	35.39	59.34	1.16	4.11
1345	2.03	2.82	31.51	65.10	1.60	1.79
1383	1.99	2.91	37.98	57.29	0.50	4.22

The value for the azulene–naphthalene isomerization obtained in the present study is equivalent to the first-order limit rate constant obtained by Brouwer and Troe,<sup>5</sup> namely,  $k_1 = 10^{12.93} \exp(-62.8 \times 10^3/\text{RT}) \text{ s}^{-1}$ . The value for the isomerization of azulene–second isomer is  $k_2 = 10^{12.42} \exp(-69.5 \times 10^3/\text{RT}) \text{ s}^{-1}$ .

### DISCUSSION

As is shown in Fig. 3, there is an excellent agreement between the rate constant deduced in this investigation

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Fig. 2. Product distribution in post-shock samples of azulene, showing the isomerization and the decomposition products. The isomerization products are the main products.



Fig. 3. A plot of log  $k_1$  vs. 1/T for the azulene  $\rightarrow$  naphthalene isomerization. There is a good agreement between the rate constant obtained in this study and the first order limit rate constant obtained at higher temperatures.



Fig. 4. A plot of log  $k_2$  vs. 1/T for the isomerization of azulene  $\rightarrow$  second isomer.

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and the first-order limit rate constant obtained at higher temperatures by Brouwer and Troe.5 They found that the experimental rate constants under their conditions were very close to the first-order limit, and a ratio of  $k_{uni}/k_{\infty} =$ 0.7 was reported at 1500 K for an overall density of 10<sup>-4</sup> mol/cm3. The experimental rate constant for the isomerization of this 18-atom molecule, in the temperature range covered in this study, is even closer to the first-order limit. Moreover, the first-order limit rate constant of Brouwer and Troe<sup>5</sup> extrapolates very well into our experimental points. It should be mentioned that the two investigations cover some six orders of magnitude variation in the rate constants without significant change in the Arrhenius parameters, namely,  $k_1 = 10^{12.93} \exp(-62.8 \times 10^3/RT) \text{ s}^{-1}$ . The extrapolation of this Arrhenius expression of  $k_1$  to a much lower temperature range (650-700 K) gives values which are more than three orders of magnitude lower than the early results of Heilbronner.<sup>1,2</sup> The reason for this disagreement is not fully understood, but it probably results from a heterogeneous free radical contribution in Heilbronner experiments.

The results obtained in this investigation clearly support a unimolecular reaction for the isomerization,<sup>4</sup> rather than a free radical mechanism, a possibility that was raised in the past by Alder et al.<sup>3</sup> This is evident from the fact that up to a temperature of about 1300 K, where the loss of azulene reaches a value of ~50%, only isomers were found as reaction products. The possibility of a radical-induced reaction mechanism for azulene– naphthalene isomerization, without appearance of any decomposition product, seems rather doubtful.

# Isomerization Mechanism

Azulene  $\rightarrow$  Naphthalene. According to the mechanism suggested by Scott and Agopian,<sup>4</sup> azulene undergoes isomerization to naphthalene via the formation of a bicyclobutane structure as an unstable intermediate ("tetracyclic triene"), followed by opening of the cyclobutane ring.

It has been suggested<sup>4,11</sup> that it is possible to describe the pathway of this bicyclobutane formation, as a Woodward-Hoffmann allowed  $[_2\pi_{supra} + _2\pi_{antara}]$ (suprafacial-antarafacial) cycloaddition, which is a cycloaddition of two  $\pi$  bonds  $C_3 = C_4$ (antara) and  $C_5 = C_6$ (supra), forming  $C_3$ - $C_5$  and  $C_4$ - $C_6$  new  $\sigma$  bonds. The opening of the cyclobutane ring in this structure by breaking the  $C_3$ - $C_4$  and  $C_5$ - $C_6$  bonds, and conversion to naphthalene, can be also established as Woodward-Hoffmann allowed  $[_2\sigma_{supra} + _2\sigma_{antara}]$  retro cycloaddition of two  $\sigma$  bonds:  $C_3$ - $C_5$ (supra) and  $C_4$ - $C_6$ (antara).

It is also possible to describe these steps by considering a second resonance structure of azulene. According to Woodward–Hoffman, the formation of the unstable



intermediate can be viewed as a supra-supra cycloaddition of the  $\pi$  bond C<sub>4</sub>=C<sub>5</sub> to C<sub>3</sub>=C<sub>2</sub>-C<sub>1</sub>=C<sub>10</sub>-C<sub>9</sub>=C<sub>8</sub>-C<sub>7</sub>=C<sub>6</sub> tetraene. Its conversion to naphthalene can be described as a supra-supra retro cycloaddition of C<sub>4</sub>-C<sub>5</sub> and C<sub>3</sub>-C<sub>2</sub>=C<sub>1</sub>-C<sub>10</sub>=C<sub>9</sub>-C<sub>8</sub>=C<sub>7</sub>-C<sub>6</sub> with breaking of the C<sub>3</sub>-C<sub>4</sub> and C<sub>5</sub>-C<sub>6</sub> bonds.

Second Isomeric Product. As has been mentioned earlier, the presence of a second isomer has been established by a GC-MS analysis (Fig. 1). A very small peak, adjacent to the naphthalene peak, was observed. However, the fact that this was a very small peak, not fully separated from naphthalene, prevented us from collecting samples for additional analyses, such as NMR and FTIR.

At this stage, we can only suggest two possible structures for this isomer. Both can be obtained from the unstable "tetracyclic triene" intermediate, which was suggested in the formation of naphthalene. Two transition states can be obtained from this intermediate, which may lead to the formation of either 1-methylene-1Hindene or 1,2,3-metheno-1H-indene,-2,3-dihydro.

The formation of 1-methylene-1H-indene can be described as a product of the same intermediate, but via a different transition state. At first the bicyclobutane structure is formed, and then it converts to 1-methylene-1H-indene by an extension and/or cleavage of the C<sub>4</sub>-C<sub>5</sub> and C<sub>3</sub>-C<sub>2</sub> bonds in the bicyclobutane structure, followed by one H-atom migration from position 3 to position 5 and forming two new  $\pi$  bonds: C<sub>5</sub>=C<sub>3</sub> and C<sub>6</sub>=C<sub>4</sub>.

1,2,3-metheno-1H-indene,-2,3-dihydro can be



formed from the "bicyclobutane" structure by breaking the same bonds,  $C_4-C_5$  and  $C_3-C_2$ , and forming two new  $\sigma$  bonds:  $C_5-C_2$  and  $C_5-C_3$ . In this case, the  $\pi$  bond  $C_1=C_2$  will be destroyed, and a  $\pi$  bond  $C_6=C_4$  will be formed. No H-atom migration is necessary for this process to take place.



**Decompositions** 

The small quantities of the following decomposition products,  $C_2H_2$ ,  $C_4H_2$ ,  $C_6H_6$ , and  $C_6H_5$ -C=CH, were found only at high temperatures (~1350 K) where the extent of azulene conversion was close to 50%. These products are the result of azulene and naphthalene decomposition. Their detailed investigation is beyond the scope of the present work.

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### **REFERENCES AND NOTES**

- (1) Heilbronner, E.; Wieland, K. Helv. Chim. Acta 1947, 30, 947.
- (2) Heilbronner, E. In Non-Benzenoid Aromatic Compounds; Ginzburg, D., Ed.; Interscience: New York, 1959, p 263.
- (3) Alder, R.W.; Whiteside, R.W.; Whittaker, G.; Wilshire, C. J. Am. Chem. Soc. 1979, 101, 629.
- (4) Scott, L.T.; Agopian, G.K. J. Am. Chem. Soc. 1977, 99, 4506.
- (5) Brouwer L.; Troe, J. Int. J. Chem. Kinet. 1988, 20, 379.
- (6) Damm, M.; Deckert, F.; Hippler, H.; Troe, J. J. Phys. Chem. 1991, 95, 2005.
- (7) Lifshitz, A.; Moran, A.; Bidani, S. Int. J. Chem. Kinet. 1987, 19, 61.
- (8) Lifshitz, A.; Tamburu, C.; Frank, P.; Just, T. J. Phys. Chem. 1993, 97, 40859.
- (9) Rodgers, A.S.; Ford, W.G.F. Int. J. Chem. Kinet. 1973, 5, 965.
- (10) Stull, D.R.; Westrum, E.F.Jr.; Sinke, G.C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.
- (11) Gajewski, J. Hydrocarbon Thermal Isomerization; Academic Press: New York, 1981, p 342.

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