

KINETICS AND THERMOCHEMISTRY OF THE REARRANGEMENT OF BENZVALENE
TO BENZENE. AN ENERGY SUFFICIENT BUT NON-CHEMILUMINESCENT REACTION

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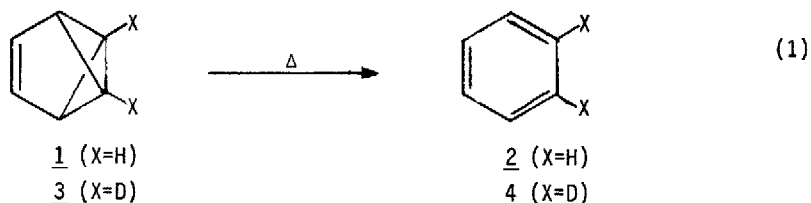
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Kinetic and thermochemical data have been reported for a number of substituted valence isomers of benzene.¹ We report here a study of the kinetics and thermochemistry of the valence isomerization of benzvalene 1 to benzene 2 (eq. 1).



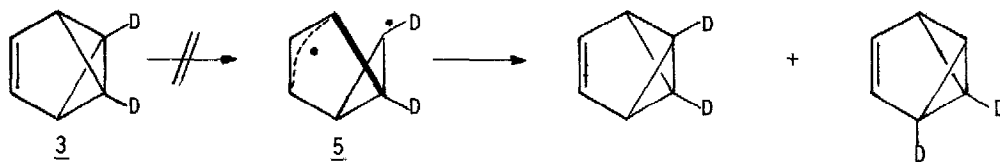
Thermolysis of 1 in *n*-heptane produces benzene quantitatively (N.M.R. analysis).^{2,3} The rearrangement is first order in the temperature range 313-330^o K. An Arrhenius plot of the data (Table 1) is linear and yields the following activation parameters: $\Delta H^\ddagger = 25.9 \pm 0.2$ kcal/mole; $\Delta S^\ddagger = 1.6 \pm 0.7$ e.u.; $E_a = 26.7 \pm 0.2$ kcal/mole; $\log A = 13.7 \pm 0.2$. Silver ion catalyzes the rearrangement of 1 \rightarrow 2 and the heat of this reaction was measured in chlorobenzene on a LKB Model 8700 precision calorimetry apparatus at 25^o C. The value obtained, adjusted for the heat of solution of benzvalene, was 67.54 ± 0.66 kcal/mole. The experimental data for which these values are based are given in Tables 1 and 3. In Table 2 available data for the valence isomers of benzene are compared.

In order to explore the mechanistic aspects of the reaction of 1 to 2 we investigated (a) whether reaction 1 is chemiluminescent and (b) the stereochemistry of the rearrangement of benzvalene-*d*₂(3).

To test for chemiluminescence the reaction 1 \rightarrow 2 was run in a solvent containing 9,10-diphenylanthracene or 9,10-dibromoanthracene, both of which have been shown to be effective traps of benzene triplet states.⁶ By comparison with the chemiluminescence of tetramethyl-1,2-dioxatene, the yield of excited benzene triplets was estimated to be less than 10⁻⁶%. This

value represents an upper limit due to chemiluminescence of the control samples. In comparison to Dewar benzene, which produces benzene triplets measurably, benzvalene is essentially non-chemiluminescent.

Thermolysis of benzvalene- d_2 was found to yield 1,2-dideuteriobenzene quantitatively (eq. 1, $X=D$). The thermal valence isomerization of 1 to 2 may be viewed as a symmetry forbidden $\sigma^2 + \sigma^2$ process and as such it may be supposed that a diradical mechanism is involved. The lack of scrambling of deuterium label requires that any biradical intermediate 5 must proceed to benzene faster than to benzvalene. In a previous photochemical study we provided evidence that both singlet and triplet diradicals derived from 1 give benzvalene with the deuterium label scrambled.⁸ The energy required to form the diradical 5 from 1 is estimated from group additivity⁹ to be ~ 40 kcal/mole, a value much higher than the observed enthalpy of activation (26 kcal/mole). A theoretical analysis of the rearrangement of 1 \rightarrow 2 has suggested that the reaction is concerted.¹⁰ Evidently, the double bond in 1 is not passive during reaction 1, but assists in the breaking of the bicyclobutane ring. The activation energy for rearrangement of bicyclobutane to 1,3-butadiene is 41 kcal/mole, a value in agreement with a biradical transition state.¹¹



The observation that Dewar benzene is chemiluminescent but that benzvalene is not deserves comment. Since reaction 1 is both more exothermic and requires a higher activation energy than the valence isomerization of Dewar benzene, reaction energetics do not preclude reaction 1 from being chemiluminescent. Thus, the sum (~ 93 kcal/mole) of the activation enthalpy (~ 26 kcal/mole) and reaction enthalpy (~ 67 kcal/mole) is well above the energy required to form benzene triplet (~ 82 kcal/mole). The mechanistic basis for the lack of chemiluminescence in reaction 1 may be sought in the reaction electronics. We consider that the most plausible explanation derives from a lack of an effective surface crossing for geometries near the transition state of reaction. The conversion of 1 to 2 is evidently an allowed reaction because the electrons of the double bond participate¹⁰ in the ring opening, making it a 6 electron process. If reaction 1 is concerted, then a strong avoided crossing between the ground surface and an excited surface is to be expected.¹² Such a situation will have the effect of lowering the energy of the transition state without affecting the energy of the triplet state at the transition state geometry; thus, the critical feature, crossing of the ground state and triplet state surfaces, which occurs for Dewar benzene and allows its rearrangement to benzene to be chemiluminescent, is evidently absent in the rearrangement of benzvalene. Of course, any explanation involving the failure of the S_1 and T_1 surfaces to cross will suffice to explain the results.

We also wish to point out that the lack of chemiluminescence, for an energy sufficient pericyclic reaction, may be used as evidence for concertedness since theory predicts a general ground state-triplet surface crossing for forbidden pericyclic reactions.^{12,13}

TABLE 1. Thermolysis of Benzvalene.

<u>Temperature</u> ($^{\circ}\text{K}$)	<u>First Order Rate Constant</u> (sec^{-1})
313.4	1.18×10^{-5}
313.4	1.19×10^{-5}
313.4	1.19×10^{-5}
326.0	6.20×10^{-5}
338.4	28.1×10^{-5}
338.4	28.1×10^{-5}

TABLE 2. Activation and Thermochemical Parameters for the Valence Isomerization of Benzene Isomers.^a

<u>Benzene Isomer</u>	<u>ΔH^{\ddagger}</u>	<u>ΔS^{\ddagger}</u>	<u>ΔH_0</u>	<u>Reference</u>
Benzvalene	25.9	1.6	-67.5	This work
Dewar Benzene	25	0.8	~ 60	(b)
Prismane	~ 27	—	< -90	(c)
3,3'-Dimethyl- bis-cyclopropene	37	—	-120	(d)

(a) Values of ΔH in kcal/mole. Values of ΔS in e.u.

(b) P. Lechtken, R. Breslow, A. H. Schmidt and N. J. Turro, J. Am. Chem. Soc., **95**, 3025 (1973).

(c) J. H. Davis, K. J. Shea, and R. G. Bergman, Angew. Chem. intern. ed. Eng., **14**, 232 (1976).

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TABLE 3. Thermochemical Data for the Isomerization of Benzvalene to Benzene.^{a,b}

<u>Raw Data</u>	<u>Heat Evolved</u> (kcal/mole)
Benzvalene (0.215N soln) \rightarrow Benzene (soln)	-67.71 \pm 0.30
<u>Corrections</u>	
(1) For solution of benzene in chlorobenzene	0.00 \pm 0.01
(2) For solution of benzvalene in chlorobenzene (cyclohexene used as model) to form a 0.215N soln	0.17 \pm 0.01
<u>Adjusted Data</u>	
Benzvalene (liq) \rightarrow Benzene (liq)	-67.54 \pm 0.30

(a) The conversion of 1 to 2 was effected by AgBF_4 catalysts at 25°C .

(b) The error limits quoted correspond to two standard deviations.

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2. The disappearance of 1 and the appearance of 2 were monitored by NMR spectroscopy. Multiple integration was employed to determine concentrations with either $\text{CH}_2\text{BrC}_6\text{H}_5$ or $\text{C}_2\text{C}_6\text{H}_3$ as an internal standard. 1 was purified by vpc on a 5% diisodecyl phthalate 1.1% triethanolamine column. The NMR tubes were treated with 1N NaOH (soaking) followed by rinsing with distilled water. The first order rate constants were determined by the least squares method. An error of the order of 4-6% in the individual run was typical.
3. Benzvalene was prepared according to the published procedure.⁴ Benzvalene- d_2 was prepared from benzvalene and D_2O .⁵ The analysis benzvalene- $\text{d}_2 \rightarrow$ 1,2-dideuteriobenzene was made by infrared analysis. By use of authentic samples, limits of < 0.5% 1,4-dideuteriobenzene and < 2% 1,3-dideuteriobenzene as products could be established.
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