# Dissociation of 1,3-Hexadiene and the Resonance Energy of the Pentadienyl Radical

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Measurements of the rate at which methane is formed in the pyrolysis of 1,3-hexadiene at temperatures over the range 694-759 K and pressures between 25 and 200 Torr show that the dissociation reaction

$$CH_{3}CH_{2}CH = CHCH = CH_{2} \rightarrow CH_{3} + CH_{2}CH = CHCH = CH_{2}$$
(1)

is a homogeneous, first-order reaction under these conditions and the rate expression is

 $\log(k_1/s^{-1}) = (15.92 \pm 0.17) - (66\,390 \pm 840)/\theta$ 

where  $\theta = 2.303 RT/cal \text{ mol}^{-1}$  (1 cal = 4.18 J).

The experimental activation energy yields for the pentadienyl radical,  $\Delta H_{f}^{2} = 45.9 \pm 1.0$  kcal mol<sup>-1</sup> at 298 K and a resonance energy of  $18.5 \pm 1.5$  kcal mol<sup>-1</sup>, assuming a value of 98.2 kcal mol<sup>-1</sup> for the primary C—H bond dissociation energy in alkanes.

The pentadienyl radical may be expected to have a somewhat higher resonance energy than that of the allyl radical in view of the greater extent of the delocalisation of the odd electron in the former. Although experimental values obtained for the resonance energy of the radical support this conclusion, they show marked variations, from  $15.4 \pm 1^1$  to  $21.7 \pm 2^2$  kcal mol<sup>-1</sup>, which may be due partly to the use of incorrect data in deriving the lower value.<sup>3</sup> The most recent estimate,<sup>3</sup> obtained from the nitric oxide catalysed isomerisation of 1,3,5-heptatriene, yielded a resonance energy of  $18.5 \pm 1.7$  kcal mol<sup>-1</sup> which appears to provide the best fit between measured and calculated rate constants for the isomerisation reaction.

Previous studies carried out in this laboratory  $^{4-6}$  have shown that the resonance energy of the allyl radical and of various substituted allyl radicals may be determined from measurements of the methane produced in the thermal decomposition of but-1-ene and its derivatives. The work described herein involves a study of the dissociation of 1,3-hexadiene following the same procedure as before. The weakest bond in this molecule must be the terminal C—C bond, the fission of which leads to the formation of a methyl radical and a resonance stabilised pentadienyl radical. A portion of the methyl radicals so produced will be converted to methane by hydrogen abstraction from the parent molecule so that measurement of the rate of formation of this product provides a means of determining the rate of the primary dissociation reaction. Hence the activation energy of the dissociation reaction may be obtained and from this the resonance energy of the pentadienyl radical can be evaluated.

## EXPERIMENTAL

#### MATERIALS

1,3-hexadiene (Aldrich) of 99 % purity was transferred to the vacuum system and after thorough outgassing was used without further purification. This material gave only a single peak when analysed by gas chromatography using a 1 m column of Chromosorb P containing 20 % di-isodecyl phthalate.

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#### APPARATUS AND PROCEDURE

The apparatus was essentially the same as that described previously <sup>5</sup> except that pressure changes in the reaction vessel during each run were monitored using a (Texas Instruments) precision pressure gauge. Methane estimations were carried out by the same procedure as before, the reaction products being transferred through traps cooled to -126 and  $-198^{\circ}$ C to a Töpler-McLeod gauge in order to effect a preliminary separation of condensable from non-condensable materials before analysis of the latter by gas chromatography. Duplicate runs showed that methane analyses were reproducible to within  $< \pm 2 \%$ .

## RESULTS

A series of runs was performed at 713 K for a range of initial pressures of 1,3hexadiene between 30 and 250 Torr, the initial pressures being estimated by extrapolation of pressure-time data to zero time. For each initial pressure, methane yields were obtained for various reaction times and the initial rate of methane formation was determined by computing a third degree polynomial equation giving the best fit with the experimental data, the initial rate being given by the coefficient of the term of power unity. A double logarithmic plot of initial rate of methane formation against pressure of reactant gave a straight line of slope  $0.99\pm0.01$ , showing that under the experimental conditions the reaction leading to the formation of methane was of first-order. Runs were subsequently performed at eight temperatures over the range 685-758.5 K and at each temperature the methane yields from a fixed pressure of  $\approx 55$  Torr 1,3-hexadiene were obtained for various reaction times. The results of this work are shown graphically in fig. 1.

Rate constants for the dissociation reaction

$$CH_{3}CH_{2}CH = CHCH = CH_{2} \rightarrow CH_{3} \cdot + \cdot CH_{2}CH = CHCH = CH_{2}$$
(1)

were obtained using the equation

$$k_{1} = \frac{k_{2} + k_{3}}{k_{3}} \left( \frac{d[CH_{4}]}{dt} \right)_{0} / [C_{6}H_{10}]_{0},$$
(2)

where  $k_2$  and  $k_3$  are the rate constants for the addition and abstraction reactions between methyl radicals and 1,3-hexadiene, respectively. From the data reported by Cvetanović and Irwin,<sup>7</sup> for a given mono-olefin, addition and abstraction reactions with methyl radicals have similar A factors and activation energy differences of the order of 0.1-0.2 kcal mol<sup>-1</sup>. For these olefins, therefore,  $k_2$  and  $k_3$  may reasonably be assumed to be equal and this assumption has been made in previous investigations 4-6 where data for the particular olefin being studied were not available. From the little information which could be found for addition and abstraction reactions between methyl radicals and dienes, the same assumption would again appear reasonable for these compounds. The Arrhenius parameters E = 4.1 kcal mol<sup>-1</sup> and log(A/dm<sup>3</sup>  $mol^{-1} s^{-1}$  = 8.2 have been obtained <sup>7</sup> for the addition of methyl radicals to 1,3-butadiene [using Kerr and Parsonage's preferred Arrhenius parameters and error limits for methyl radical abstraction from 2-methylpropane,8 these become  $E = 4.5 \pm 1.0$  kcal mol<sup>-1</sup> and log(A/dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) =  $8.3 \pm 0.6$ ] and these figures are close to the values  $E = 5.5 \pm 0.3$  kcal mol<sup>-1</sup> and  $\log(A/dm^3 \text{ mol}^{-1} \text{ s}^{-1}) = 8.5 \pm 0.2$ for the metathetical reaction between methyl radicals and 1,4-cyclohexadiene.<sup>9</sup> Rate constants for the dissociation of 1,3-hexadiene have, therefore, been derived on the assumption that, under the experimental conditions,  $k_2 = k_3$ . The values obtained are given in table 1 and these yield the rate expression

$$\log(k_1/s^{-1}) = 15.92 \pm 0.17 - (66\ 390 \pm 560)/\theta$$

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FIG. 1.—Plots of methane against time for the decomposition of 55 Torr 1,3-hexadiene. +, packed reaction vessel at 725.5 K;  $\bigcirc$ , unpacked reaction vessel: (a) 685, (b) 694, (c) 703, (d) 713, (e) 725, (f) 737, (g) 748 and (h) 758.5 K.

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T/	/K	$(d[CH_4]/dt)_0/10^{-4}$ Torr s <sup>-1</sup>	$[C_6H_{10}]_0/Torr$	$k_1/10^{-6}  \mathrm{s}^{-1}$	
68	5	1.44	55.4	5.21	
69	4	2.81	55.4	10.1	
70	3	5.69	55.6	20.5	
71	3			$37.2 + 2.0^{b}$	
72	5	23.4	55.5	85.3	
72	5.5 <sup>a</sup>	24.6	57.6	85.5	
73	7	45,5	56.3	161	
74	8	92.0	56.8	324	
75	8.5	177	56.3	630	

 TABLE 1.—INITIAL RATES OF FORMATION OF METHANE AND RATE CONSTANTS

 FOR THE DISSOCIATION OF 1,3-HEXADIENE

<sup>*a*</sup> Data obtained using a packed reaction vessel. <sup>*b*</sup> From least-squares estimate of intercept of plot of  $\log(d[CH_4]/dt)_0$  against  $\log p$ .

where  $\theta = 2.303 RT/cal \text{ mol}^{-1}$  and the quoted error limits correspond to the estimated standard deviation.

Since the activation energy for the dissociation of 1,3-hexadiene is of prime interest in this work and the possibility of a difference of 1 kcal mol<sup>-1</sup> between  $E_2$  and  $E_3$ cannot be ruled out, the effect of such a difference on the activation energy has been determined and it was found to change  $E_1$  by no more than 0.65 kcal mol<sup>-1</sup>, whilst the A factor remains at virtually the same value. To take account of the possible error in  $E_1$  arising from the assumed equality of  $E_2$  and  $E_3$ , the error limits quoted for  $E_1$  may, therefore, be more reasonably quoted as  $\pm 840$  cal mol<sup>-1</sup>.

A further assumption involved in the derivation of eqn (2) is that radicals formed from addition and abstraction reactions between methyl radicals and 1,3-hexadiene do not subsequently dissociate to reform methyl radicals. As pointed out previously,<sup>6</sup> for mono-olefins, this assumption is strictly valid only at infinitely high pressures. With dienes, the situation is somewhat different since both addition and abstraction reactions must lead preferentially to the formation of resonance stabilised species having rates of dissociation which, over the experimental pressure range, will be negligible in comparison with those of further addition and abstraction reactions. The addition of methyl radicals to 1,3-hexadiene must occur mainly at carbon atoms 1 and 4 and, as with 1,3-butadiene, should require a lower activation energy than is generally found for the addition of methyl to mono-olefins where resonance stabilised addition products are not formed. Although metathetical reactions between methyl radicals and both mono-olefins and dienes can produce resonance stabilised radicals, activation energies for reactions with the latter should again be generally lower, since these can yield radicals which are stabilised by a greater degree of delocalisation, *i.e.* over five carbon atoms rather than over three.

The rate expression for  $k_1$  given above yields a value of  $83.2 \times 10^{-6} \, \text{s}^{-1}$  for  $k_1$  at 725.5 K as compared with the measured value of  $85.5 \times 10^{-6} \, \text{s}^{-1}$  obtained from experiments carried out using the packed reaction vessel at this temperature. The close agreement between these two figures indicates that in the decomposition of 1,3-hexadiene, primary methane is formed by an entirely homogeneous process.

### DISCUSSION

In the pyrolysis of 1,3-hexadiene, methane is formed, as with other olefins, by both primary and secondary processes; this leads to methane against time curves which at temperatures below 723 K show an increase in the rate of formation of methane with time. Measurements of the rate of formation of the primary methane from the initial slopes of the methane against time curves indicate that this product is formed by an homogeneous first-order reaction under the experimental conditions employed.

The reliability of the assumptions made in evaluating  $k_1$ , the rate constant for the dissociation reaction, may be checked by comparing the experimental A factor with that derived theoretically from thermodynamic data. The entropy and specific heat data given in table 2 were derived using group additivity methods <sup>10</sup> together with the procedures described in ref. (11) and these values yield for reaction (1) at 700 K,  $\Delta S_c^{\circ} = 28.09$  cal K<sup>-1</sup> mol<sup>-1</sup> for a standard state of 1 mol dm<sup>-3</sup>.

The rate constant for the recombination of pentadienyl radicals has not been measured but may be estimated by assuming a linear relationship between the molecular weight of a free radical and the logarithm of its recombination rate constant.<sup>13</sup> Taking values of 10.42,<sup>14</sup> 9.9<sup>15</sup> and 9.6<sup>16</sup> for  $\log(k_r/dm^3 mol^{-1} s^{-1})$  of  $\cdot CH_3$ ,  $\cdot C_3H_5$  and  $\cdot C_4H_7$ , respectively, leads to a value of 9.4 for  $\log(k_r/dm^3 mol^{-1} s^{-1})$  for pentadienyl radicals and hence, using the geometric mean rule,  $\log(k_{-1}/dm^3 mol^{-1}$ 

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 $s^{-1}$ ) = 10.2. Assuming reaction (-1) occurs with zero activation energy, this recombination rate corresponds to  $\Delta S_c^{\pm} = -17.5 \text{ cal K}^{-1} \text{ mol}^{-1}$  and hence for the forward reaction  $\Delta S_c^{\pm} = 10.8 \text{ cal K}^{-1} \text{ mol}^{-1}$  at 700 K and the theoretical A factor has a value of  $10^{15.9} \text{ s}^{-1}$ , in excellent agreement with the experimental value. The observation that for this, as for most of the other systems studied by the same procedure,<sup>4-6</sup> there is good agreement between experimental and calculated A factors, strongly supports the conclusion that the assumptions made in deriving the rate constants for the dissociation reactions are reasonable.

species	$\Delta H_{\rm f298}^{\circ}$ /kcal mol <sup>-1</sup>	$S^{\circ}_{p298}$ /cal K <sup>-1</sup> mol <sup>-1</sup>	C°p298 /cal K <sup>-1</sup> mol <sup>-1</sup>	$C^{\circ}_{p700}$ /cal K <sup>-1</sup> mol <sup>-1</sup>
C <sub>5</sub> H <sub>8</sub>	18.3	76.6	24.4	44.0
$C_6H_{10}$	13.6	86.4	29.5	54.4
CH <sub>3</sub>	34.8 <sup><i>a</i></sup>	46.4	8.3	11.8
$C_5H_7$	45.9 <sup>b</sup>	74.8	23.5	43.5

TABLE 2.—THERMODYNAMIC	DATA	FOR	RADICALS	AND	MOLECULES				
relevant to reaction (1)									

<sup>a</sup> From value reported by Chupka [ref. (12)]; <sup>b</sup> see text.

The activation energy for the dissociation reaction yields, for reaction (1),  $\Delta H_{298}^{\circ} = 67.1 \pm 0.8$  kcal mol<sup>-1</sup>, again assuming an activation energy of zero for the reverse reaction. This leads to a value of  $\Delta H_{\rm f}^{\circ} = 45.9 \pm 1.0$  kcal mol<sup>-1</sup> for the pentadienyl radical at 298 K. Thus, for the reaction

$$CH_{3}CH = CHCH = CH_{2} \rightarrow H \cdot + \cdot CH_{2}CH = CHCH = CH_{2}, \quad (3)$$

 $\Delta H_{298}^{\circ} = 79.7 \pm 1.1$  kcal mol<sup>-1</sup>, which, when compared with the long accepted value of  $98.2 \pm 1$  kcal mol<sup>-1</sup> for the dissociation energy of a primary C—H bond in alkanes,<sup>17</sup> yields a value of  $18.5 \pm 1.5$  kcal mol<sup>-1</sup> for the resonance energy of the pentadienyl radical. This value, being in exact agreement with that obtained by Egger and Jola,<sup>3</sup> must add confidence to these two estimates.

Recently reported values for  $\Delta H_{\rm f}^{\circ}$  (t-Bu) which are higher than the previously accepted figure have led to a reassessment of bond dissociation energies in alkanes<sup>18</sup> and from this a value of  $100.5 \pm 1$  kcal mol<sup>-1</sup> has been proposed for the dissociation energy of a primary C—H bond. Using this value, the resonance energy of the pentadienyl radical becomes  $20.8 \pm 1.3$  kcal mol<sup>-1</sup>, a figure which cannot be directly compared with earlier estimates, all of which were derived from the lower primary C—H bond dissociation energy.

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