Thermal Unimolecular Decomposition of 1-Ethylcyclohexa-1,4-diene, 1,2-Dimethylcyclohexa-1,4-diene and Bicyclo[4,3,0]nona-1$^{(6)}$,3-diene

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The pyrolysis of 1-ethylcyclohexa-1,4-diene has been studied from 316 to 379°C in the gas phase at pressures of around 10 Torr. Under these conditions, in an aged reaction vessel, the reaction was strictly first order, and the products, hydrogen and ethylbenzene were formed quantitatively. The rate constants yielded the Arrhenius equation:

$$\log k_1/\text{s}^{-1} = 13.12 \pm 0.09 - 45\,870 \pm 250 \text{ cal mol}^{-1}/2.303\, RT$$

i.e.,

$$\log k_1/\text{s}^{-1} = 13.12 \pm 0.09 - 191\,930 \pm 1030 \text{ J mol}^{-1}/2.303\, RT.$$

The pyrolysis of 1,2-dimethylcyclohexa-1,4-diene in the temperature range 296 to 354°C was found to yield only hydrogen and *o*-xylene. At pressures between 0.25 and 5.4 Torr which was the range studied, the reaction was strictly first order and the rate constants obtained yielded the Arrhenius equation:

$$\log k_2/\text{s}^{-1} = 12.54 \pm 0.03 - 43\,720 \pm 80 \text{ cal mol}^{-1}/2.303\, RT$$

i.e.,

$$\log k_2/\text{s}^{-1} = 12.54 \pm 0.03 - 182\,920 \pm 320 \text{ J mol}^{-1}/2.303\, RT.$$

The pyrolysis of bicyclo[4,3,0]nona-1$^{(6)}$,3-diene yielded hydrogen and bicyclo[4,3,0]nona-1,3,5-triene (1,2-dihydroindene) as the only products. In the temperature range 346 to 408°C and at pressure above 0.8 Torr the decomposition was first order and the rate constants obtained yielded the Arrhenius equation:

$$\log k_3/\text{s}^{-1} = 12.95 \pm 0.16 - 48\,580 \pm 470 \text{ cal mol}^{-1}/2.303\, RT$$

i.e.,

$$\log k_3/\text{s}^{-1} = 12.95 \pm 0.16 - 203\,260 \pm 1960 \text{ J mol}^{-1}/2.303\, RT.$$

The results obtained in this work are compared with those obtained for the pyrolyses of other cyclohexa-1,4-dienes.

The thermal elimination of hydrogen from cyclohexa-1,4-diene is an orbital symmetry allowed unimolecular process. In many systems where the observed processes are orbital symmetry forbidden it is possible to postulate biradical reaction mechanisms and in this fashion not only rationalize the observed products but also correlate the energetics of whole series of reactions of similar types. As an example it is possible to predict semi-quantitatively the effect of substituents. Such systems include the valence bond isomerizations of cyclopropanes and possibly the thermal decomposition of cyclobutanes. An intermediate situation occurs in the hydrogen halide elimination reaction in the gas phase pyrolysis of alkyl halides. Here the reaction, which is orbital symmetry forbidden, probably occurs by a concerted process involving a highly polar transition complex. Again it is possible to correlate substituent effects in a very satisfactory manner. For the allowed unimolecular processes, far less has so far proved to be possible in the way of rationalizing substituent effects, and indeed these have often proved to be rather small, as for example in the Cope rearrangement or the isomerization of simple cyclobutenes. The present work is part of a programme directed towards obtaining precise data for several series of allowed unimolecular reactions, in the hope that the factors which influence the energetics will emerge.

EXPERIMENTAL

MATERIALS

1-Ethylcyclohexa-1,4-diene was obtained from Chemical Samples Co. (Columbus, Ohio). It was purified by preparative gas chromatography using a 2 m by 6 mm column packed with Chromosorb P coated with 15 % w/w silicone oil (MS 550) and operated at 70°C. The sample was dried over sodium and was better than 99.8 % pure.

1,2-Dimethylcyclohexa-1,4-diene was supplied by Prof. L. A. Paquette. It had been prepared by the Birch reduction of *o*-xylene and still contained a little of the latter compound. It was purified by preparative gas chromatography using a 7.8 m by 4.4 mm (i.d.) column packed with 60-80 mesh Chromosorb P coated with 20 % w/w di(2-cyanoethyl) ether. The final purity was better than 99.9 %.

Bicyclo[4,3,0]nona-$1^{(6)}$,3-diene was obtained from the Aldrich Chemical Co. Inc. Purification was by gas chromatography using a 1.8 m by 4.4 nm (i.d.) column containing Chromosorb P coated with 20 % w/w Carbowax 4000. The material so obtained was better than 99.8 % pure.

APPARATUS

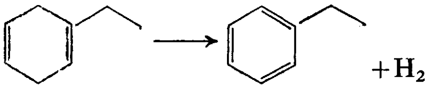
The kinetic apparatus was essentially the same as that described earlier.[1] Pressures were measured either with a transducer whose active element was an unbounded strain gauge (Bell and Howell type 4–327–0003) or using a Texas Instruments precision pressure gauge model 145 (quartz spiral).

Analysis was by gas chromatography using Perkin-Elmer F11 and 452 instruments equipped with gas sampling valves. Signals from the flame ionization detector (F.I.D.) were fed to a chart recorder and integrated.

RESULTS

1-ETHYLCYCLOHEXA-1,4-DIENE

The thermal decomposition of 1-ethylcyclohexa-1,4-diene was investigated in the temperature range 316 to 379°C. The products were ethylbenzene and hydrogen.



The progress of the reaction was followed by pressure change. Preliminary experiments indicated that the rate constant was independent of pressure above 5 Torr, and subsequent work was carried out with initial reactant pressures of around 10 Torr. The gas handling line and gas pipettes were maintained at 90°C to minimize absorption problems. In this system, with the strain gauge transducer, the dead space was less than 0.4 % and no correction was made for it.

TABLE 1.—RATE CONTANTS FOR THE DECOMPOSITION OF 1-ETHYLCYCLOHEXA-1,4-DIENE

T/°C	316.2	321.0	328.6	338.1	338.3
$10^4\ k_1/s^{-1}$	1.310	1.734	2.780	5.239	5.235
T/°C	348.0	358.1	366.5	373.9	379.4
$10^4\ k_1/s^{-1}$	9.594	17.47	26.79	42.24	57.40

(The data are quoted without rounding off, however, it is not implied that all the figures are significant.)

At least 2 complete runs were carried out at each of 10 temperatures. Plots of log $(2P_0 - P_t)$ against time were linear to greater than 50 % decomposition and rate constants were obtained from these plots by the method of least squares. The average values obtained are shown in table 1. Agreement between duplicate runs was better than 1 % and the standard deviation in the rate constant at the 6 highest temperatures was less than ±0.2 %. The results in table 1 gave a good Arrhenius plot which yielded the following equation;

$$\log k_1/\mathrm{s}^{-1} = 13.12 \pm 0.09 - 45\,870 \pm 250 \text{ cal mol}^{-1}/2.303\ \boldsymbol{RT}$$

or

$$\log k_1/\mathrm{s}^{-1} = 13.12 \pm 0.09 - 191\,930 \pm 1030 \text{ J mol}^{-1}/2.303\ \boldsymbol{RT}$$

(The errors quoted are standard deviations and probably merely indicate that the results are highly reproducible with little random error.)

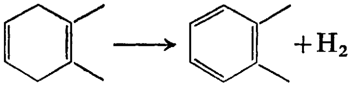
Runs were carried out at 366.5°C in a packed reaction vessel with a surface to volume ratio approximately 25 times that of the unpacked vessel. These runs yielded a rate constant within 1 % of that obtained in the unpacked vessel. There is therefore unlikely to be any appreciable heterogeneous component of the reaction.

A complete series of runs at 343.5°C was followed analytically by gas chromatography, using a Perkin-Elmer 452 instrument with a 100 m polypropyleneglycol capillary column operated at 80°C. Signals from the F.I.D. were integrated electronically. Calibration factors determined by injection of liquid mixtures, for ethylbenzene and 1-ethylcyclohexa-1,4-diene were identical within experimental error.

A plot of the logarithm of undecomposed 1-ethylcyclohexa-1,4-diene against time was linear to 70 % decomposition and from this plot the rate constant was determined and found to be within 2 % of that calculated from the Arrhenius equation (which was based on pressure data alone).

1,2-DIMETHYLCYCLOHEXA-1,4-DIENE

In the temperature range 296 to 354°C, 1,2-dimethylcyclohexa-1,4-diene decomposes to yield *o*-xylene and hydrogen.



Initial experiments showed the rate constant to be independent of pressure in the range 0.25 to 5.4 Torr. All subsequent rate determinations were carried out with an initial reactant pressure of between 3 and 4 Torr. The reaction was followed by pressure measurements using a quartz spiral gauge (Texas Instruments) and because the dead space (of about 1 %) could not be ignored corrections were made using methods due to Robinson [2] and Allen.[3] With the Robinson method it is necessary to plot log $(P_\infty - P_0)$ against time and with the Allen method log P_r against time (where $P_r = P\{2(P_0/P)^\alpha - 1\}$ and α is the ratio of the total volume of the system, after temperature corrections, to the volume of the reaction zone). Both plots were linear to over 70 % reaction. Throughout the Allen method yielded rate constants some 3 % greater than the Robinson method.

Four runs were carried out at each of nine temperatures and a further two runs at another temperature. The results obtained are given in table 2. Arrhenius plots from the results in table 2 are the same within experimental error from both methods of evaluating the rate constants viz.,

$$\log k_2/\mathrm{s}^{-1} = 12.54 \pm 0.03 - 43\,720 \pm 80 \text{ cal mol}^{-1}/2.303\ \boldsymbol{RT}$$

or

$$\log k_2/\mathrm{s}^{-1} = 12.54 \pm 0.03 - 182\,920 \pm 320\ \mathrm{J\ mol^{-1}}/2.303\ \boldsymbol{RT}$$

(Robinson method)

$$\log k_2/\mathrm{s}^{-1} = 12.54 \pm 0.03 - 43\,670 \pm 80\ \mathrm{cal\ mol^{-1}}/2.303\ \boldsymbol{RT}$$

or

$$\log k_2/\mathrm{s}^{-1} = 12.54 \pm 0.03 - 182\,710 \pm 350\ \mathrm{J\ mol^{-1}}/2.303\ \boldsymbol{RT}$$

(Allen method)

TABLE 2.—RATE CONSTANTS FOR THE DECOMPOSITION OF 1,2-DIMETHYLCYCLOHEXA-1,4-DIENE

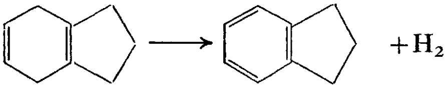
Robinson method					
T/°C	295.6	300.4	305.3	310.4	317.6
10^4k_2/s^{-1}	0.562	0.772	1.05	1.46	2.34
	0.543	0.769	1.06	1.48	2.37
	0.556	0.771	1.05		2.34
	0.554	0.775	1.07		2.32
T/°C	322.3	337.3	339.6	347.6	352.7
$10^4\ k_2$/s^{-1}	3.08	7.76	8.68	14.2	19.3
	3.15	7.56	8.71	14.2	19.3
	3.06	7.74	8.78	14.2	18.9
	3.13	7.83	8.87	14.3	19.1
Allen method					
T/°C	295.6	300.4	305.3	310.4	317.6
$10^4\ k_2$/s^{-1}	0.582	0.801	1.08	1.51	2.44
	0.565	0.803	1.10	1.52	2.46
	0.579	0.805	1.10		2.43
	0.575	0.806	1.11		2.41
T/°C	322.3	337.3	339.6	347.6	352.7
$10^4\ k_2$/s^{-1}	3 21	8.02	8.98	14.6	20.0
	3.26	7.82	9.03	14.7	20.0
	3.17	8.00	9.11	14.8	19.6
	3.24	8.13	9.22	14.7	19.9

Two complete series of runs at 346.8°C and 311.9°C were followed by gas chromatographic analysis. These runs yielded rate constants within 1 % of those obtained by pressure measurements (using the Robinson method of calculation). Another series of runs at 335.7°C was carried out in a packed reaction vessel having a surface to volume ratio about 10 times that of the unpacked vessel. These were followed by gas chromatographic analysis and the rate constant obtained was within 3 % of the mean value computed from both Arrhenius equations. There can be no appreciable heterogeneous component of the reaction.

BICYCLO[4,3,0]NONA-$1^{(6)}$,3-DIENE

The thermal decomposition of bicyclo[4,3,0]nona-$1^{(6)}$,3-diene was investigated within the temperature range 346.1 to 407.9°C, using the same experimental system as for 1,2-dimethylcyclohexa-1,4-diene. Because of the low volatility of the compound it was necessary to work with initial reactant pressures of 0.8 Torr and below.

However, preliminary runs followed by gas chromatographic analysis, showed that the rate of reaction was identical with an initial reactant pressure of 0.8 Torr in the presence and absence of added nitrogen (100 Torr). In both cases the reaction was strictly first order. Subsequent runs were carried out with initial reactant pressures between 0.6 and 0.8 Torr and followed by pressure changes. In the system used the dead space was about 2 % and rate constants were determined from plots using the Robinson method. These plots were linear to greater than 60 % decomposition. The gas chromatographic analysis showed the only reaction products to be bicyclo[4,3,0]nona-1,3,5-triene (1,2-dihydroindene) and hydrogen.



The reproducibility obtained for the values of the rate constants in this study were very appreciably poorer than for the other two compounds. Probably this was in a large part due to the necessity of working with such low reactant pressures and also

TABLE 3.—RATE CONSTANTS FOR THE DECOMPOSITION OF BICYCLO[4,3,0]NONA-$1^{(6)}$,3-DIENE

T/°C	346.1	351.3	361.1	367.0	374.7	376.8
$10^4\ k_3/s^{-1}$	0.666	0.833	1.645	2.320	3.675	4.197
T/°C	383.2	388.0	388.7	394.2	399.1	
$10^4\ k_3/s^{-1}$	5.67	8.273	8.86	10.62	14.81	
T/°C	399.6	407.9				
$10^4 k_3/s^{-1}$	14.53	17.95				

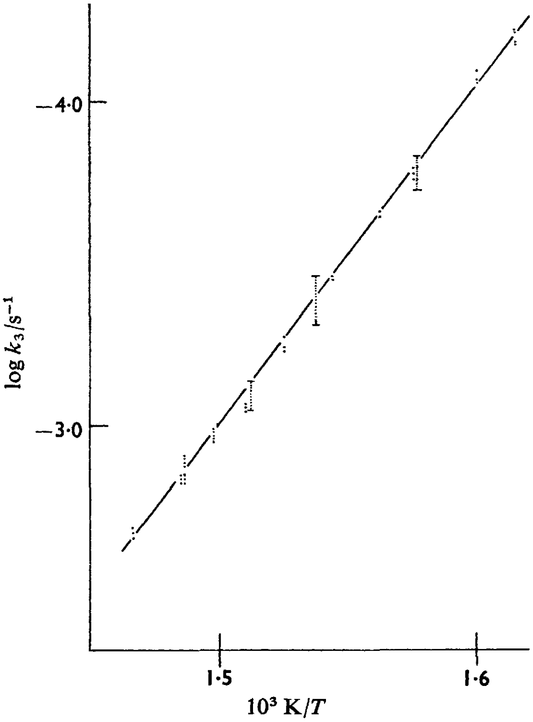


FIG. 1.—Arrhenius plot for decomposition of bicyclo[4,3,0]nona-$1^{(6)}$,3-diene.

problems associated with absorption, always a source of error with relatively non-volatile reactants and products. In an attempt to reduce random errors a large number of rate studies were carried out and in all 77 complete runs at 14 different temperatures were followed. Only the mean value of the rate constant is reported for each temperature in table 3, however, all the points were used in calculation of the Arrhenius parameters. The Arrhenius equation obtained in this manner was

$$\log k_3/\mathrm{s}^{-1} = 12.95 \pm 0.16 - 48\ 580 \pm 470\ \mathrm{cal\ mol}^{-1}/2.303\ RT$$

or

$$\log k_3/\mathrm{s}^{-1} = 12.95 \pm 0.16 - 203\ 260 \pm 1960\ \mathrm{J\ mol}^{-1}/2.303\ RT$$

The rate constants are also shown in an Arrhenius plot in fig. 1. (Note corresponding figures for the two other cyclohexadienes are not shown since the deviations of the points from a straight line cannot be indicated on any reasonably sized plot.)

If, instead of all the rate constants, we use the mean values at each temperature (as shown in table 3) then the Arrhenius equation data yield is:

$$\log k_3/\mathrm{s}^{-1} = 12.97 \pm 0.22 - 48{,}660 \pm 640\ \mathrm{cal\ mol}^{1-}/2.303\ RT$$

which is the same, within much less than the standard deviations, as the equation obtained using the individual rate constants.

At 388.7°C a kinetic series of runs was carried out using gas chromatographic analysis. The rate constant obtained, $8.72 \times 10^{-4}\ \mathrm{s}^{-1}$ compares with the mean value determined by pressure change of $8.86 \times 10^{-4}\ \mathrm{s}^{-1}$ (the value from the Arrhenius equation is $8.2 \times 10^{-4}\ \mathrm{s}^{-1}$) and the agreement must be considered satisfactory considering the rather large experimental errors. Similarly, a run in a packed reaction vessel, followed by gas chromatographic analysis, gave a rate constant identical within experimental error to that obtained in the unpacked vessel.

DISCUSSION

The rates at which cyclohexa-1,4-dienes substituted in either the 1 or both the 1 and 2 positions by alkyl groups eliminate hydrogen are very similar. Under these circumstances relatively small systematic errors can produce far larger changes in the derived parameters, A and E of the Arrhenius equation than in the rate constants themselves. This can lead to apparent relationships between changes in A and E.

TABLE 4.—RELATIVE RATES OF DECOMPOSITION AND FREE ENERGIES OF ACTIVATION OF SOME CYCLOHEXA-1,4-DIENES AT 600 K

compound	$\Delta G^{\ddagger}(600)$ / kJ mol^{-1}	$\Delta G^{\ddagger}(600)$ / kcal mol^{-1}	relative rates at 600 K	ref.
cyclohexa-1,4-diene (CHD)	191.7	46.82	1.0	4
1-methyl CHD	191.7	45.82	1.0	5
1-ethyl CHD	191.9	45.86	1.0	this work
1,2-dimethyl CHD	189.7	45.33	1.5_5	this work
bicyclononadiene	204.9	48.98	0.07	this work

In such situations there is much to be said for comparing the effect of substitution on the rate constants themselves or more conveniently the values of the free energies of activation. The available data are shown in table 4, where the rate of decomposition of cyclohexa-1,4-diene itself at 600 K is taken as unity.

It is immediately apparent that there is no difference between the values for $\Delta G^{\ddagger}(600)$ for the first three compounds in table 4 and even the value for 1,2-dimethylcyclohexa-1,4-diene differs only by a very small amount. The elimination of hydrogen from these molecules, which is " orbital symmetry allowed ", must occur by an appreciable distortion of the cyclohexadiene ring making it into a very non-planar boat form. Examination of models suggests that in the case of 1,2-dimethylcyclohexa-1,4-diene this results in an increase in the methyl-methyl distance and hence a reduction in the methyl-methyl repulsion. The effect is small but may be sufficient to account for the slightly reduced value of $\Delta G^{\ddagger}$ and hence the rate acceleration by about 50 %. Exactly the same explanation may be applied to the bicyclononadiene decomposition. Here the distortions required to reach the configuration of the activated complex will *increase* the strain in the 5 membered ring and hence results in a relatively large increase in $\Delta G^{\ddagger}$. It is also possible that some of the increase results in part from slightly lower resonance energy than the product is likely to have as compared with benzene or toluene. On this simple model it is possible to rationalize the observed relative rates. As in some other systems, we find here also, that concerted processes appear less sensitive to substituent effects than non-concerted processes, especially when the substituents do not introduce any new steric problems.

We thank Prof. L. A. Paquette for the sample of 1,2-dimethylcyclohexa-1,4-diene and the S.R.C. for the award of Research Studentships to A.T.C. and R.G.H.

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