View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Cope Rearrangements of Cis and Trans hepta-1,5-diene and 3-Methylhexa-1,5-diene

BY H. M. FREY AND R. K. SOLLY

Chemistry Dept., Reading University

Received 15*th January*, 1968

The isomerization of trans hepta-1,5-diene (I) to cis hepta-1,5-diene (III) occurs via 3-methylhexa-1,5-diene (II). Both reactions which are reversible and unimolecular are examples of the Cope rearrangement. No direct cis-trans isomerization occurs. The Arrhenius equations for all four rate constants have been determined in the temperature range 220-300°C. Equilibrium values have been measured up to 390°C and hence enthalpy and entropy differences evaluated. The *A* factors for the isomerizations are in reasonable agreement with those expected for a cyclic transition complex and are also similar to values obtained for other Cope rearrangements. The reasons for the discrepancies between the present work and a recent study of this system are considered.

The Cope rearrangement of 1,5-dienes have been well documented as unimolecular reactions.[1] It has been shown by Doering and Roth,[2] and verified by Hill and Gilman,[3] that the rearrangement occurs via a six-membered cyclic transition state in the chair form, which is described as " four-centre " due to the orbital overlap between four carbon atoms. There is still little precise kinetic information about these reactions in the gas phase. O'Neal and Benson [4] have estimated the Arrhenius pre-exponential factors for a series of unimolecular reactions proceeding via cyclic transitions states. The predicted value for the Cope rearrangement of 1,1,6,6-tetradeuteriohexa-1,5-diene to 3,3,4,4-tetradeuteriohexa-1,5-diene is in excellent agreement with that obtained experimentally, but the agreement is poor for the reversible rearrangement of 3-methylhexa-1,5-diene to hepta-1,5-diene reported by Amano and Uchiyama.[5] This latter reaction has been re-investigated to see whether the experimental results or the approximations involved in estimating the *A* factors are in error.

EXPERIMENTAL

3-Methylhexa-1,5-diene was obtained commercially and purified by preparative gas chromatography using a 25 ft × ¼ in. column packed with 30-60 mesh Chromosorb P containing 20 % w/w of di-(2-cyanoethyl)-ether. Analysis of the product by gas chromatography (di-(2-cyanoethyl)-ether and silicone oil) showed it to be better than 99·99 % pure.

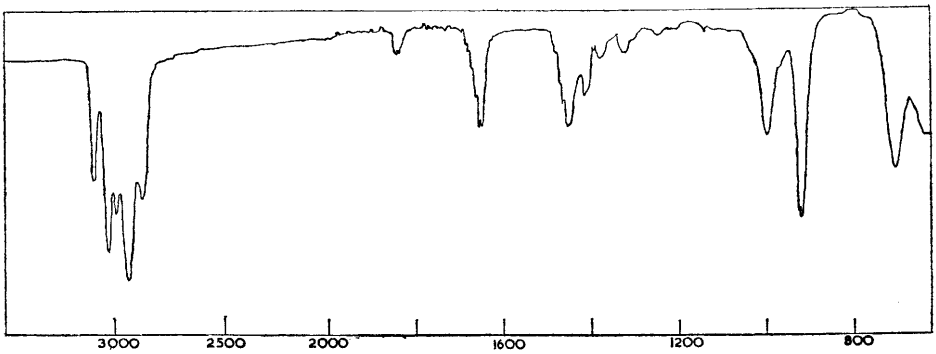
Cis and trans hepta-1,5-diene were obtained by the gas-phase pyrolysis of 3-methylhexa-1,5-diene at 300°C and purified by gas chromatography. Identification was by infra-red spectra (fig. 1). The cis isomer shows a characteristic absorption at 700 cm^{-1} which is absent in the trans compound. The infra-red spectrum for the trans hepta-1,5-diene reported by Amano and Uchiyama does not show any absorption at 700 cm^{-1} but there is a peak at ~1000 cm^{-1} which is absent from our trans compound, but is similar to a peak at 1008 cm^{-1} (medium intensity) which is present in the cis isomer.

Kinetic measurements were carried out in a static system, which was similar in all essential details to one described previously.[6] Pyrolyses were carried out in two 150 ml spherical Pyrex vessels immersed in a molten salt bath. The use of two vessels enabled kinetic measurements to be made at the same time as equilibrium studies. These were carried out indiscriminately in either vessel and the rates were independent of which vessel was used. Runs were also carried out in a cylindrical Pyrex vessel packed with Pyrex tubes. This packed vessel had a surface-to-volume ratio some 8 times greater than the unpacked vessels.

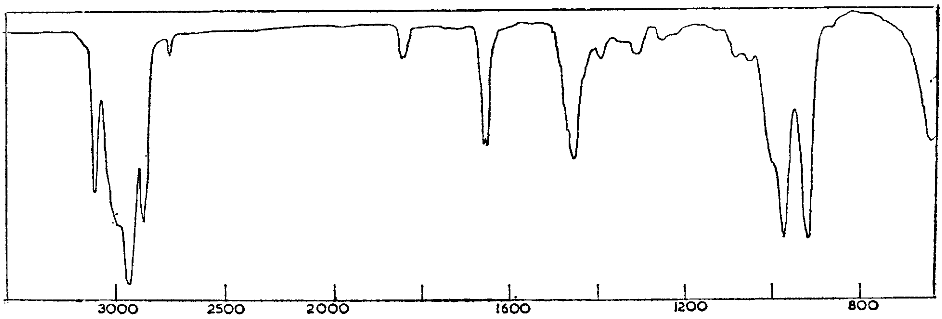
View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Analysis was by gas chromatography using an Aerograph Hi-Fi 500C instrument with a hydrogen-flame detector and fitted with a gas-sampling valve. The best separation of reactant and products was obtained using a 16 ft × $\frac{1}{8}$ in. stainless steel column packed with 60-80 mesh Chromosorb P containing 20% w/w of di-2-cyanoethyl-ether. Signals from the detector were integrated (Ball and disc integrator) and all analyses were performed in duplicate.



cis-1,5-heptadiene

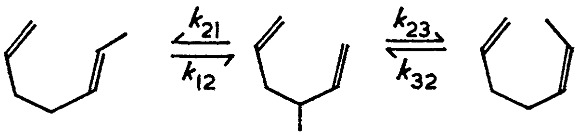


trans-1,5-heptadiene

FIG. 1.—Infra-red spectra of cis and trans-1,5-heptadiene.

RESULTS

Preliminary experiments showed that 3-methylhexa-1,5-diene isomerized to both cis and trans hepta-1,5-diene by simultaneous first order reversible reactions. There was no direct cis→trans isomerization.



(I) (II) (III)

Kinetic studies were carried out between 220 and 300°C and equilibrium studies extended up to 390°C. No significant quantities of other rearrangement or fragmentation products were observed. Thus at 300°C pyrolysis for a time equal to 44 half-lives of the slowest reaction (k_{32}) which is equivalent to over 300 half-lives of reaction k_{21} produced less than 0·5% of material other than I, II and III. Even at 390°C, equilibrium studies carried out for a time equivalent to 14 half-lives of the slowest reaction showed the presence of only 0·2% of products other than I, II, and III.

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Results obtained in the packed reaction vessel were identical within experimental error with those obtained in the unpacked vessels. There can thus be no appreciable heterogeneous component of the reaction. The majority of runs were with an initial reactant pressure of 2 mm. However, variations of the initial pressure from 0·2 to 100 mm produced no change in the analytical results. Hence the rate constants are independent of pressure in this range. All the evidence is thus consistent with these reactions being true unimolecular isomerizations.

If one starts from either cis or trans hepta-1,5-diene then the reaction scheme is that for consecutive reversible first-order reactions. The solution of these equations has been discussed previously.[7] Thus starting from pure trans hepta-1,5-diene (I) we obtain

$$\mathrm{I} = \mathrm{I}^\circ\left\{\frac{k_{21}k_{32}}{\lambda_2\lambda_3}+\frac{k_{12}(\lambda_2-k_{23}-k_{32})}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)+\frac{k_{12}(k_{23}+k_{32}-\lambda_3)}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\},$$

$$\mathrm{II} = \mathrm{I}^\circ\left\{\frac{k_{12}k_{32}}{\lambda_2\lambda_3}+\frac{k_{12}(k_{32}-\lambda_2)}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)+\frac{k_{12}(\lambda_3-k_{32})}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\},$$

$$\mathrm{III} = \mathrm{I}^\circ\left\{\frac{k_{12}k_{23}}{\lambda_2\lambda_3}+\frac{k_{12}k_{23}}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)-\frac{k_{12}k_{23}}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\},$$

where $\lambda_2 = \frac{1}{2}(p+q)$ and $\lambda_3 = \frac{1}{2}(p-q)$,

$$p = (k_{12}+k_{21}+k_{23}+k_{32})$$
$$q = [p^2-4(k_{12}k_{23}+k_{21}k_{32}+k_{12}k_{32})]^{\frac{1}{2}}.$$

Starting from pure cis hepta-1,5-diene (III) it is only necessary to interchange I and III and I° by III° and the relevant rate constants.

In the majority of runs pure 3-methylhexa-1,5-diene (II) was used as the starting material. The system is then one of simultaneous rather than consecutive reactions. These equations can be solved in a similar manner and yield

$$\mathrm{I} = \mathrm{II}^\circ\left\{\frac{k_{21}k_{32}}{\lambda_2\lambda_3}+\frac{k_{21}(k_{32}-\lambda_2)}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)-\frac{k_{21}(k_{32}-\lambda_3)}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\},$$

$$\mathrm{II} = \mathrm{II}^\circ\left\{\frac{k_{12}k_{32}}{\lambda_2\lambda_3}+\frac{(k_{32}-\lambda_2)(k_{12}-\lambda_2)}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)-\frac{(k_{12}-\lambda_3)(k_{32}-\lambda_3)}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\},$$

$$\mathrm{III} = \mathrm{II}^\circ\left\{\frac{k_{12}k_{23}}{\lambda_2\lambda_3}+\frac{k_{23}(k_{12}-\lambda_2)}{\lambda_2(\lambda_2-\lambda_3)}\exp(-\lambda_2 t)-\frac{k_{23}(k_{12}-\lambda_3)}{\lambda_3(\lambda_2-\lambda_3)}\exp(-\lambda_3 t)\right\}.$$

The problem of obtaining the individual rate constants from the analytical data has been discussed by Vriens.[8] We have preferred to use the above equations and obtain the rate constants by an adaptation of the method suggested by Aldous and Mills [9] for refining force constants to fit experimentally observed vibrational frequencies (an analogous problem). Approximate values of the rate constants were obtained from initial rate studies and equilibrium constants, and an error vector was constructed from the deviations between the computed and experimental concentrations. A correction vector was obtained for the original rate constants so that the sum of the squares of the errors was reduced. This process was repeated until the correction vector was zero and the sum of the squares of the errors a minimum. All calculations were carried out on an Elliott 803 computer. A good fit of the experimental data with the computed concentration curves was obtained. In fig. 2, 3, 4 this is shown for cases starting with either pure I, II or III. (The graphs shown are calculated from the rate constants and plotted using a " curve plotter ".)

The calculated rate constants at various temperatures are shown in Table 1.

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

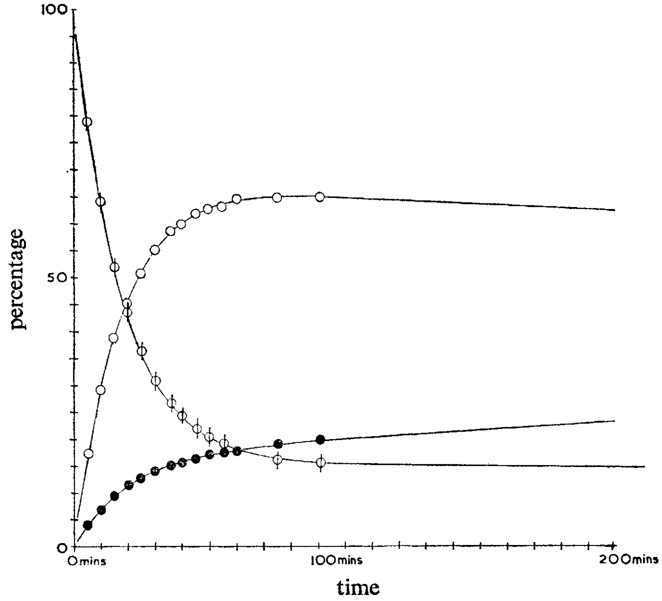


FIG. 2.—Progress curves starting from 3-methylhexa-1,5-diene, at 270·3°C.

○, trans hepta-1,5-diene; ●, cis hepta-1,5-diene; ⦶, 3-methylhexa-1,5-diene. Solid curve is calculated from rate constants.

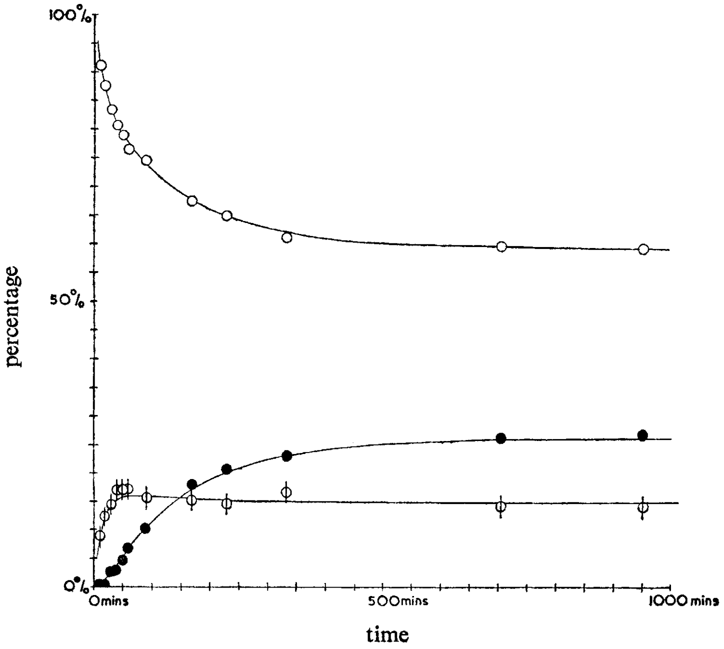


FIG. 3.—Progress curves starting from trans hepta-1,5-diene, at 274·7°C.

○, trans hepta-1,5-diene; ●, cis hepta-1,5-diene; ⦶, 3-methylhexa-1,5-diene. Solid curve is calculated from rate constants.

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Arrhenius plots of the data given in table 1 gave good straight lines, but there were large deviations from the line for the lowest two temperature values of k_{32}. In these cases the value of k_{32} was recalculated by another procedure. This used the values of k_{23} and the values of the equilibrium constants at these two temperatures. In turn the values of the equilibrium constants were obtained by extrapolation from a plot of the logarithms of the equilibrium constants against the reciprocal of the absolute temperature (van't Hoff plot). This procedure gave a much better fit to the line.

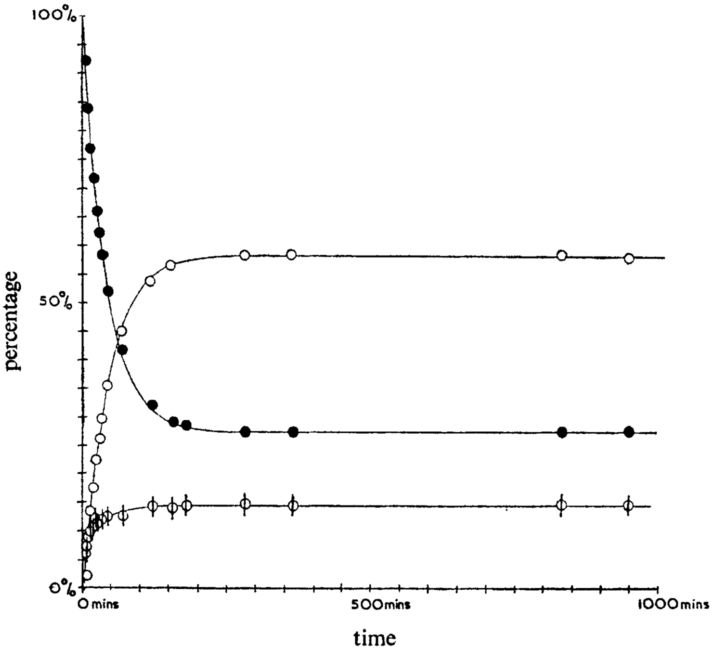


Fig. 4.—Progress curves starting from cis hepta-1,5-diene, at 294·3°C.

○ trans hepta-1,5-diene; ●, cis hepta-1,5-diene; ⏀, 3-methylhexa-1,5-diene. Solid curve is calculated from rate constants.

Table 1.—Rate constants

temp. °C	$k \times 10^5$ (sec^{-1})			
	k_{21}	k_{12}	k_{23}	k_{32}
220·1	2·646	0·586	0·525	0·309 0·252*
230·8	5·468	1·165	1·062	0·503 0·518*
238·8	8·795	1·970	2·051	0·979
249·2	17·55	4·116	4·099	2·020
260·7	35·11	8·252	8·161	4·179
270·3	63·60	15·60	14·94	7·979
274·7	71·47	17·79	17·76	10·08†
279·9	111·1	27·77	26·73	14·46
290·1	191·3	48·03	45·83	24·68
294·3	256·4	63·70	63·65	33·75‡
298·8	327·6	81·58	80·47	42·59

* calculated values from k_{23} and equilibrium constants. † starting from trans-1,5-heptadiene.
‡ starting from cis-1,5-heptadiene.

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Least squares calculations of the Arrhenius parameters gave the following equations;

$$
\begin{aligned}
k_{21} &= 10^{10\cdot 55 \pm 0\cdot 16} \exp\left(-34{,}196 \pm 386/RT\right)\text{sec}^{-1},\\
k_{12} &= 10^{10\cdot 39 \pm 0\cdot 14} \exp\left(-35{,}335 \pm 348/RT\right)\text{sec}^{-1},\\
k_{23} &= 10^{10\cdot 54 \pm 0\cdot 13} \exp\left(-35{,}718 \pm 316/RT\right)\text{sec}^{-1},\\
k_{32} &= 10^{10\cdot 66 \pm 0\cdot 08} \exp\left(-36{,}718 \pm 196/RT\right)\text{sec}^{-1}.
\end{aligned}
$$

The errors quoted are standard deviations calculated by normal statistical procedures.

The method employed for obtaining the rate constants is believed to give more reliable results than the method proposed by Vriens[8] since no special statistical weighting is placed on the values of the equilibrium composition as compared with data obtained before equilibrium is reached. In fact, it is not necessary to follow a reaction to equilibrium provided sufficient data for high conversions are included. If sufficient data at high conversion are not included then the Jacobian matrix, which is set up to determine the error vector may become ill-defined, particularly in respect of the smallest rate constant. This is believed to be the reason why the values for k_{32} at the lowest two temperatures were in error. To a lesser extent this may also apply to the next high pair of temperatures, and consequently the values of the equilibrium constants calculated from the rate constants at these temperatures show greater deviations on the van't Hoff plot than calculated values at higher temperatures.

TABLE 2.—EQUILIBRIUM CONSTANTS

temp. °C	$K\left(\frac{\text{I}}{\text{II}}\right)$	$K\left(\frac{\text{III}}{\text{II}}\right)$	$K\left(\frac{\text{I}}{\text{III}}\right)$
238·8	4·464	2·096	2·129
243·6	4·591	2·028	2·263‡
243·6	4·579	2·039	2·246†
249·2	4·265	2·029	2·102*
260·7	4·273	1·956	2·185*
270·3	4·077	1·873	2·177*
274·7	4·017	1·762	2·280*†
279·9	4·001	1·849	2·164*
290·1	3·983	1·857	2·145*
294·3	4·026	1·886	2·135*‡
298·8	4·016	1·889	2·126*
309·9	3·874	1·870	2·071
319·8	3·913	1·882	2·080
329·5	3·761	1·833	2·052
340·1	3·742	1·796	2·084
351·3	3·643	1·753	2·078
356·1	3·644	1·785	2·041†
361·8	3·550	1·751	2·027
372·2	3·513	1·743	2·015
382·8	3·437	1·725	1·992
387·7	3·499	1·719	2·035‡
393·5	3·353	1·706	1·965

* calculated from rate constants. † starting from trans-1,5-heptadiene. ‡ starting from cis-1,5-heptadiene.

Equilibrium constants were obtained directly by analysis of equilibrium concentrations at temperatures where rate constants could no longer be obtained with the "static technique" employed. At each temperature up to 390°C duplicate analyses were carried out on mixtures which had been pyrolyzed for three different times, to ensure that equilibrium had been reached. The average values obtained at each temperature are shown in table 2.

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

Van't Hoff plots of this data yielded the following enthalpy and entropy differences,

$H_{\rm I}-H_{\rm II} = -1{\cdot}28\pm0{\cdot}06$ kcal mole^{-1}; $S_{\rm I}-S_{\rm II}$ $0{\cdot}51\pm0{\cdot}06$ cal/mole deg.
$H_{\rm III}-H_{\rm II} = -0{\cdot}76\pm0{\cdot}05$ kcal mole^{-1}; $S_{\rm III}-S_{\rm II}$ $-0{\cdot}07\pm0{\cdot}09$ cal/mole deg.
$H_{\rm I}-H_{\rm III} = -0{\cdot}51\pm0{\cdot}03$ kcal mole^{-1}; $S_{\rm I}-S_{\rm III}$ $0{\cdot}60\pm0{\cdot}06$ cal/mole deg.

These values are all within the statistical errors for the same parameters derived from the rate equations. However, since the equilibrium constants have been obtained over a much greater temperature range the values from this source are more accurate.

DISCUSSION

The energies of activation of this series of reactions fall in the range 34-37 kcal mole^{-1}. These values are considerably less than the 56 kcal mole^{-1} reported for the rupture of hexa-1,5-diene to two allyl radicals.[10] This is undoubtedly due to the considerable orbital overlap in the cyclic transition state. The results are in good agreement with the value of 35·5 kcal mole^{-1} reported for the isomerization of 1,1,6,6-tetradeuteriohexa-1,5-diene.[11]

The difference of 1·5 kcal mole^{-1} between the energies of activation for the formation of I and III from II must arise from the stereochemical structures of the transition complex and most probably represents the energy difference between the chair form of the complex with either the methyl group in the equatorial or axial position. The free energy difference of about 1 kcal mole^{-1} in favour of a trans methyl group as compared with a cis methyl group reported by Doering and Roth [2] may also be interpreted as the energy difference between an axial and equatorial methyl. This assumes no difference in entropy of activation as was found in the present work. Further support for this interpretation for a difference of between 1 and 1·5 kcal mole^{-1} between these forms of the transition complex comes from the observed difference of 1·4 kcal mole^{-1} in the activation energies for the isomerizations of I and III to II, whereas the enthalpy difference between I and III is only 0·5 kcal mole^{-1}.

The A factors for the isomerizations of I and III to II were $10^{10{\cdot}39}$ and $10^{10{\cdot}66}$ respectively. (For the reverse reactions the A factors are identical within experimental error.) Assuming a transmission coefficient of unity this is equivalent to entropies of activation at 600°K of $-14{\cdot}37$ and $-13{\cdot}13$ cal/mole deg. respectively. Because the reverse reactions have the same A factor we must ascribe this difference in entropy of activation of 1·0 cal/mole deg. to the difference in entropies between the cis and trans hepta-1,5-dienes. This value compares favourably with the more accurate value of 0·60 cal/mole deg. determined from the van't Hoff plot.

O'Neal and Benson [4] have calculated the entropies of activation for 4- and 6-centre unimolecular reactions. The particular case of the Cope rearrangement is considered. In these calculations the main contribution to $\Delta S^{\ddagger}$ comes from the replacement of hindered internal rotations (present in the reactant) by various vibrational modes in the cyclic transition complex. The calculation is sensitive to the barriers postulated for the internal rotations. For 1,1,6,6-tetradeuteriohexa-1,5-diene the agreement between the experimental and calculated A factor is excellent. There is also good agreement between experimental and calculated values for a number of isomerizations of vinyl allyl ethers, a closely related transformation. However the discrepancy of 6·7 cal/mole deg. between the previous experimental data for 3-methylhexa-1,5-diene and the calculated value appeared to be well outside the error limits of the calculations. Using the A factor obtained in the present work the discrepancy is 3·4 cal/mole deg., i.e., about half the previous difference. The discrepancy between the calculated and experimental entropy of activation for the isomerization of cis hepta-1,3-diene to 3-methylhexa-1,5-diene is only 2 cal/mole deg.,

View Article Online

Published on 01 January 1968. Downloaded by Queen Mary, University of London on 9/17/2019 3:25:15 PM.

but this is due to factors not taken account of in the calculation (a reduction in the entropy of the reactant). While we cannot rule out the possibility that the experimental data are in error the discrepancy is well outside the probable error limits of the work and we believe that it is more likely that the calculations are in error. The entropy of activation for the isomerization of hepta-1,2,6-triene to 3-methylenehexa-1,5-diene [1] is 5·2 cal/mole deg. greater than the calculated value. It is possible that higher frequencies should be assigned to the torsional vibrational modes in the activated complex. Only further experimental work on related systems can settle this point.

The results obtained in this study differ considerably from those obtained by Amano and Uchiyama.[5] They reported that the isomerization of 3-methylhexa-1,5-diene gave predominantly trans hepta-1,5-diene with an A factor of $10^{9 \cdot 84}$ and the reverse reaction had an A factor of $10^{9 \cdot 09}$. Both processes were found to have the same energy of activation (32·5 kcal mole^{-1}). The reason for the difference between the two sets of results arises from the failure of the earlier workers to resolve the cis and trans hepta-1,5-dienes adequately on their chromatographic column and this led to an underestimate of the extent of the formation of the cis isomer. In addition, they obtained no variation of equilibrium constant with temperature. This again arises from the same basic analytical fault. Because of the nature of the kinetics of the system, times taken to reach compositions close to true equilibrium become a large multiple of the number of half-lives of the fastest reaction. We calculate that at 210°C the time taken to reach a composition within 0·1% of the equilibrium concentrations requires 59, 55 and 66 days starting from pure I, II or III respectively. Thus at these lower temperatures, Amano and Uchiyama had never reached an equilibrium composition. The failure to find a variation of equilibrium constant with temperature led to the result that both forward and reverse reactions had the same energy of activation.

We thank the Hydrocarbon Research Panel of the Institute of Petroleum for a grant in support of this work.

---

[1] H. M. Frey and D. H. Lister, *J. Chem. Soc. A*, 1967, 26.
[2] W. V. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67; *Angew. Chem.* (*Int. Ed.*), 1963, **2**, 115.
[3] R. K. Hill and N. W. Gilman, *Chem. Comm.*, 1967, 619.
[4] H. E. O'Neal and S. W. Benson, *J. Physic. Chem.*, 1967, **71**, 2903.
[5] A. Amano and M. Uchiyama, *J. Physic. Chem.*, 1965, **69**, 1278.
[6] R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 1964, 5578.
[7] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (New York, John Wiley, 1953), p. 162.
[8] G. N. Vriens, *Ind. Eng. Chem.*, 1954, **46**, 669.
[9] J. Aldous and I. M. Mills, *Spectrochim. Acta*, 1962, **18**, 1073.
[10] R. J. Akers and J. J. Throssell, *Trans. Faraday Soc.*, 1967, **63**, 124.
[11] V. Toscano and W. von E. Doering, from ref. (4).