# 885. *The Thermal Unimolecular Isomerisation of* cis-*2-Methylpenta-1,3-diene*

By H. M. Frey and R. J. Ellis

*cis*-2-Methylpenta-1,3-diene undergoes reversible thermal isomerisation to 4-methylpenta-1,3-diene. In the range 200—237°, in an " aged " vessel, the reaction is homogeneous and first-order, and the rate constant is independent of pressure from 2 to 15 mm. Rate constants at various temperatures in the above range fit the Arrhenius equation:

$$k_{2\cdot4} = 10^{11\cdot24}\exp(-32{,}760/RT)\ \text{sec.}^{-1}.$$

Measurement of the equilibrium constant at six temperatures in the range 200—404° gave the enthalpy change $\Delta H_{2\cdot4} = -3\cdot43$ kcal. mole$^{-1}$.

The probable transition state for this isomerisation is discussed, and the results are compared with those for the thermal isomerisation of *cis*-1-methyl-2-vinylcyclopropane.

In addition to the three well established types of thermal unimolecular isomerisation of cyclopropanes, *viz.*, alkylcyclopropanes to olefins,[1] *cis–trans*-isomerisation,[2] and, for some unsaturated cyclopropanes, ring-expansion to yield cyclopentenes,[3] we recently reported a rearrangement involving a 1,5-hydrogen shift. Thus, *cis*-1-methyl-2-vinylcyclopropane yields *cis*-hexa-1,4-diene by a unimolecular process.[4] The suggested transition state for this reaction was formulated by analogy with the isomerisation of *cis*-2-methylpenta-1,3-diene to 4-methylpenta-1,3-diene, although the latter reaction has been studied qualitatively only at much higher temperatures.[5] We have investigated this isomerisation in detail to determine the kinetics and obtain useful thermochemical data.

## Experimental

*Cis*-2-Methylpenta-1,3-diene was prepared by the photosensitised isomerisation of the *trans*-diene followed by the separation of the *cis*-form. A 4 : 1 mixture of *trans*-2-methylpenta-1,3-diene and 4-methylpenta-1,3-diene was prepared by dehydration of the commercially available hexylene glycol (2-methylpentane-2,4-diol) by refluxing [6] it with aniline hydrobromide.

A solution of the diene mixture (10 ml.) and acetophenone (10 ml.) in isopentane (600 ml.) was irradiated in a Pyrex vessel with a Hanovia 500 U.V.S. mercury lamp. After about 3 hr., a photostationary state of roughly equal amounts of *cis*- and *trans*-2-methylpenta-1,3-diene was produced.[7] The 4-methylpenta-1,3-diene was unaffected by the irradiation. After removal of the isopentane by fractional distillation, the diene mixture was refluxed with a slight excess of dimethyl fumarate for 2 hr.; the *trans*-diene gave the Diels–Alder adduct quantitatively, whereas the *cis*-compound was unchanged. After reflux the unreacted dienes were removed by distillation, to give a mixture of only *cis*-2-methylpenta-1,3-diene and 4-methylpenta-1,3-diene. Pure *cis*-2-methylpenta-1,3-diene was obtained by preparative gas chromatography using 1,2-di-(2-cyanoethoxy)ethane [8] as the liquid phase.

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[1] T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; M. C. Flowers and H. M. Frey, *J.*, 1962, 1157; *Proc. Roy. Soc.*, 1961, *A*, **260**, 424.

[2] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996; M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122; H. M. Frey and D. C. Marshall, *J.*, 1963, 5717; C. S. Elliot and H. M. Frey, *J.*, 1964, 900.

[3] M. C. Flowers and H. M. Frey, *J.*, 1961, 3547; C. A. Wellington, *J. Phys. Chem.*, 1962, **66**, 1671; H. M. Frey and D. C. Marshall, *J.*, 1962, 3981; R. J. Ellis and H. M. Frey, *J.*, 1964, 959, 4188.

[4] R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 1964, 221; *J.*, 1964, 5578.

[5] J. Wolinsky, B. Chollar, and M. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 2775.

[6] M. G. Dupont and M. Darmon, *Bull. Soc. chim. France*, 1939, **6**, 1208.

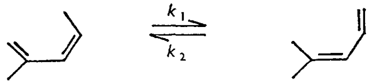
[7] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[8] H. A. Brunson and T. W. Riemer, *J. Amer. Chem. Soc.*, 1943, **65**, 23.

The kinetic apparatus, pyrolysis procedure, and analytical technique were essentially the same as described previously.[4]

## RESULTS AND DISCUSSION

In the range 197—237° *cis*-2-methylpenta-1,3-diene undergoes a first-order reversible isomerisation to yield an equilibrium mixture of *cis*-2-methylpenta-1,3-diene and 4-methylpenta-1,3-diene. There is also a much slower isomerisation to *trans*-2-methylpenta-1,3-diene, but in the above temperature range this is so slow that even when the major reaction has reached equilibrium (after 10 half-lives) there is less than 2% of the *trans*-compound.



Runs were made at pressures from 2 to 15 mm. at 225·2°; each was for 15 minutes, and in all cases the amount of decomposition was 54%, within experimental error. The rate constants are thus independent of pressure in this range.

For a first-order reversible reaction,

$$(k_1 + k_2) = (2{\cdot}303/t)\log_{10}\{x_e/(x_e - x)\}$$

where $x$ is the amount of product at time $t$ and $x_e$ the equilibrium amount. Hence, a plot of $\log_{10}\{x_e/(x_e - x)\}$ against time should be linear. Values of the equilibrium constant (and hence $x_e$) were determined from 200 to 404° by analysis of reaction mixtures that had been heated for at least 10 half-lives at each temperature. The values obtained together with the calculated free-energy differences are shown in Table 1. With the exception of the lowest temperature, a plot of $\log_{10}K$ against the reciprocal of the absolute temperature gave an excellent straight line, and even in the case of the lowest temperature the deviation corresponds to an analytical error of only 0·4%. From the slope of the plot the enthalpy difference between the *cis*-2-methylpenta-1,3-diene and the 4-methylpenta-1,3-diene is —3·43 kcal./mole.

TABLE 1

Equilibrium concentrations of 4-methylpenta-1,3-diene

| Temperature (°c) | 200·1 | 236·8 | 255·8 | 302·8 | 350·0 | 403·8 |
|---|---|---|---|---|---|---|
| % 4-Methylpenta-1,3-diene | 92·66 | 91·08 | 90·0 | 87·17 | 84·23 | 81·15 |
| $K$ | 12·62 | 10·21 | 9·00 | 6·794 | 5·341 | 4·305 |
| $-\Delta G^*$ (kcal./mole) | 2·38 | 2·35 | 2·31 | 2·19 | 2·11 | 1·96 |

The rate constants for the isomerisation were determined at ten temperatures. A full kinetic run was also performed in a packed reaction vessel (surface to volume ratio ten times that of the unpacked vessel). The results obtained in the packed vessel fitted exactly on the Arrhenius plot determined from the unpacked vessel, and the final values of the Arrhenius parameters have been computed using these data. The values of the rate constants, determined from the linear plots of $\log_{10}\{x_e/(x_e - x)\}$ against time by the method of least-squares, together with the appropriate values of the equilibrium constant, are given in Table 2. A plot of log $k_1$ against the reciprocal of the absolute temperature gave

TABLE 2

Rate constants and equilibrium constants

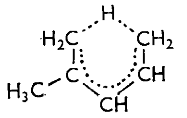
| Temp. (°c) | 236·8 | 231·5 | 229·0 | 223·8 | 223·4 * | 222·8 | 218·5 | 214·4 | 210·0 | 204·8 | 200·1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $10^4(k_1 + k_2)$ | 17·26 | 12·23 | 10·79 | 7·381 | 7·050 | 6·819 | 5·386 | 3·779 | 2·879 | 1·938 | 1·402 |
| $K$ | 10·21 | 10·59 | 10·79 | 11·19 | 11·22 | 11·25 | 11·59 | 11·99 | 12·42 | 12·88 | 13·30 |
| $10^4k_1$ | 15·72 | 11·17 | 9·870 | 6·775 | 6·473 | 6·262 | 4·958 | 3·488 | 2·665 | 1·798 | 1·304 |

* Packed reaction vessel.

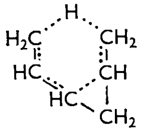
a good straight line from which the Arrhenius equation was calculated by the method of least-squares:

$$k_1 = 10^{11\cdot 24}\exp(-32{,}760/\boldsymbol{R}T)\ \text{sec.}^{-1}.$$

All the experimental evidence indicates that the isomerisation is truly unimolecular. The Arrhenius parameters are very similar to those obtained for *cis*-1-methyl-2-vinylcyclopropane, *viz.*, $\log_{10} A = 11\cdot 03$, $E_A = 31\cdot 24$ kcal. The magnitude of the frequency factors, and the similarity of the two values, and the fact that the isomerisation of the cyclopropane yields only the *cis*-diene all suggest that the same cyclic transition state is involved in both reactions. The most likely transition states are (I) and (II). The six-membered ring is



(I)



(II)

similar to that postulated in the cases of the pyrolyses of vinyl ethyl ether [9] and various esters.[10] The " $A$ " factors yield a value for the entropy of activation $\Delta S^{\ddagger}\sim -8$ e.u. (We have taken $A = (\boldsymbol{k}T/\boldsymbol{h})\exp \Delta S^{\ddagger}/\boldsymbol{R}$, whereas there is more theoretical justification for the equation $A = (e\boldsymbol{k}T/\boldsymbol{h})\exp \Delta S^{\ddagger}/\boldsymbol{R}$, when the $A$ factor is calculated from the Arrhenius plot. In recent literature the former equation has been the more frequently used, but often the equation used has not been stated. It would be helpful if authors specified their method of calculating entropies of activation.)

A negative entropy of activation is to be expected with the transition state suggested, but the value is perhaps high. The major factor must be the loss of two internal (free) rotations in going from the reactant to the cyclic transition complex. However, this cannot produce a loss of much more than 6 e.u.; thus, a further loss of 2 e.u. is unaccounted for. If the theoretically more satisfactory equation is used to calculate $\Delta S^{\ddagger}$ the discrepancy becomes greater. In addition, there is a further factor which has not been considered and that relates to path degeneracy. In the isomerisations being considered this has a value of 3 (since there are three methyl hydrogens that can move). Thus, the actual difference between the value of $\Delta S^{\ddagger}$ expected and that calculated may be as much as 4·5 e.u. It is interesting that the decomposition of ethyl vinyl ether also has a larger (negative) entropy of activation than expected from a simple consideration of the ring complex.[9] That the loss of free rotation is the principal cause of the negative entropy of activation is shown unambiguously in the thermal reversible isomerisation of bicyclo[5,1,0]oct-2-ene to cycloocta-1,4-diene.[11] Here there is no free rotation in the bicyclic compound and the Arrhenius equation for the reaction, $(k_1 + k_2) = 10^{13\cdot 34}\exp(-38{,}600/\boldsymbol{R}T)$ sec.$^{-1}$, shows that, as expected, the $A$ factor is normal. The higher energy of activation for the isomerisation ($\sim$6 kcal.) than that in the present study is also to be expected, since the transition complex in the case of the bicyclic compound is considerably more strained.

The values of the equilibrium constants for the isomerisation of *cis*-2-methylpenta-1,3-diene to the 4-methyl compound yield $\Delta H_{2\cdot 4} = -3\cdot 43$ kcal., and $\Delta S_{2\cdot 4} = 2\cdot 18$ e.u. These values seem remarkably high. In preliminary experiments on the catalysed isomerisation between 4-methylpenta-1,3-diene and *trans*-2-methylpenta-1,3-diene an equilibrium mixture of the 4-methyl compound (42%) and the 2-methyl compound (58%) was obtained at 300°K. This corresponds to a $\Delta G$ of only −190 cal./mole; the corresponding enthalpy change is probably also small. Thus, the enthalpy difference between *cis*- and *trans*-2-methylpenta-1,3-diene is probably not far from 3·4 kcal. The corresponding value [12] for *cis*- and *trans*-penta-1,3-diene is only 1·07 kcal. A much higher value of the

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[9] A. T. Blades and G. W. Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1039.

[10] A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366.

[11] W. Grimme, *Chem. Ber.*, 1965, **98**, 756.

[12] K. W. Egger and S. W. Benson, personal communication.

enthalpy difference is to be expected in the present case owing to the methyl–methyl interaction in the favoured *S-trans*-conformation of the *cis*-isomer, an interaction which is absent in the unsubstituted pentadienes.

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