## 588. *The Kinetics and Mechanism of the Thermal Cyclisation of Hexa*-1,cis-3,5-*triene to Cyclohexa*-1,3-*diene.*

By K. E. Lewis and H. Steiner.

This cyclisation proceeds quantitatively in the vapour phase at 117—190°. It is unimolecular, $k = (7{\cdot}15 \pm 5{\cdot}2) \times 10^{11} \exp -(29{\cdot}900 \pm 500)/\boldsymbol{R}T$ sec.$^{-1}$. The frequency factor of this internal diene isomerisation indicates a cyclic transition configuration which agrees with the most widely accepted mechanism of diene associations. However, comparison of the activation energy with that of the diene association of ethylene and butadiene, which involves similar reaction centres, shows that the cyclic and symmetrical transition configuration, generally assumed for diene associations, requires modification. A cyclic but asymmetrical transition configuration is suggested which is supported by calculations of the activation energies of both cyclisation and association reactions using the Polanyi–Evans method of intersecting potential energy surfaces.

The photochemical scission of cyclohexa-1,3-diene and of cyclohexadiene derivatives to give hexa-1,3,5-triene and hexatriene derivatives, respectively, has been observed.[1, 2] Cyclohexadiene is formed, amongst other products, when hexa-1,3,5-triene is irradiated by ultraviolet (u.v.) light.[3] We found that the purely thermal cyclisation of hexa-1,*cis*-3,5-triene to cyclohexa-1,3-diene is practically quantitative at 120—190°.

The cyclisation of hexatriene is an internal diene rearrangement. An important difference from the usual type of diene associations is the formation of only one, not two, new bonds during reaction. Thus we hoped that investigation of the kinetics and mechanism of the triene cyclisation would throw light on the mechanism of diene reactions in general, which in spite of much work and discussion has not finally been clarified.

Since the thermal cyclisation of hexa-1,*cis*-3,5-triene had not previously been observed, we first investigated the general chemistry and particularly the products of the reaction. After we had established that the reaction gave practically quantitatively only cyclohexa-1,3-diene, the kinetics were investigated in the gas phase. It is a straightforward unimolecular reaction.

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[1] De Kock, Minnard, and Havinga, *Rec. Trav. chim.*, 1960, **79**, 922.
[2] Srinivasan, *J. Amer. Chem. Soc.*, 1960, **82**, 5063.
[3] Srinivasan, *J. Amer. Chem. Soc.*, 1961, **83**, 2806.

## EXPERIMENTAL

*Materials*.—cis/trans-*Hexa*-1,3,5-*triene*. The synthetic route of Hwa, Sims, and de Benneville [4] for the preparation of the isomeric mixture of hexa-1,3,5-triene *via* the hexa-1,3-dienylbenzylammonium bromide was followed; yield 40%, ratio *cis* : *trans*, 3 : 7.

*Hexa*-1,cis-3,5-*triene*. This was separated by treatment with maleic anhydride,[4] repeated until all the *trans*-isomer had been removed, as shown by the infrared (i.r.) spectrum and by vapour phase chromatography on ββ′-oxydipropionitrile. The purified *cis*-isomer had b. p. 38—39°/200 mm. Hg; $n_D^{25}$ 1·5050. Micro-hydrogenation over Adams catalyst at room temperature and pressure absorbed the calculated amount of hydrogen. The i.r. spectrum was identical with that reported,[4,5] but the extinction coefficients of the peak maxima of the u.v. spectrum were different [4] (see Table 1).

TABLE 1.

Values of $10^4\varepsilon$.

| Compound | | | mμ | Ref. |
|---|---|---|---|---|
| Cyclohexa-1,3-diene ........................ | 0·430 | | 257 | *a* |
| | 0·458 | | 258 | 1 |
| | 245 mμ | 255 mμ | 265 mμ | |
| *cis/trans*-Hexa-1,3,5-triene .............. | 3·06 | 4·10 | 3·38 | *a* |
| | 3·5 | 4·8 | 3·9 | 4 |
| *trans*-Isomer ................................ | 3·3 | 4·5 | 3·5 | *a* |
| | 3·6 | 5·3 | 4·4 | 4 |
| | 3·4 | 4·3 | 3·5 | 8 |
| | 3·40 | 4·80 | 4·06 | *b* |
| *cis*-Isomer .................................. | 2·70 | 3·50 | 2·72 | *a* |
| | 2·9 | 4·1 | 3·0 | 4 |

Solvent 2,2,4-trimethylpentane, except n-hexane in ref. *b*.

*a*. This Paper. *b*. Schwartzman, Shakelford, and Michalowicz, *J. Org. Chem.*, 1962, **27**, 1631.

The *cis*-isomer for kinetic experiments after being degassed several times was stored in solid CO$_2$–methanol. No change in properties was observed even after several weeks' storage.

*Hexa*-1,trans-3,5-*triene*. This was obtained from the isomeric mixture by treatment of an ether solution with iodine followed by distillation, b. p. 38°/20 mm. Hg; $n_D^{25}$ 1·5079.

*Cyclohexa*-1,3-*diene*. Cyclohexene was β-brominated [6] with *N*-bromosuccinimide,[7] followed by dehydrobromination with quinoline under nitrogen. The product was purified through the silver nitrate addition compound.[1] Absence of benzene and cyclohexene was shown by vapour phase chromatography. The i.r. spectrum was identical to that published in the A.P.I. Index.

*Apparatus*.—A static system, evacuable to $10^{-5}$ mm. Hg, was used. Three Pyrex reaction vessels, each of *ca*. 100 ml., were situated in separate pockets of a vapour bath. One vessel was packed with Pyrex tubes, increasing the surface : volume ratio 9 times. The temperature of the bath, heated by the vapour of a boiling organic liquid chosen within the range of 110 to 192°, could be maintained to ±0·3° (the temperature gradient over the length of a reaction vessel was 0·3°), and measured to 0·05° by a copper–constantan thermocouple and potentiometer. The reaction vessels were filled to a known pressure through a thermostatted vessel. Reaction pressures above the vapour pressure of *cis*-hexatriene at room temperature were obtained in a fourth reaction vessel by filling through a heated Toepler pump. The product was collected in individual traps connected to weighed Pyrex ampoules.

*Analysis*.—U.v. spectroscopy was found suitable for quantitative analysis of a mixture of cyclohexa-1,3-diene and hexa-1,*cis*-3,5-triene. Vapour phase chromatography proved unsatisfactory, several stationary phases failing to resolve them completely.

Cyclohexa-1,3-diene absorbs with a single peak at 257 mμ, while hexa-1,3,5-triene has three peaks at 245, 255, and 265 mμ. The course of isomerisation could thus be followed by a change of the three peaks to a single peak in the 240—270 mμ range. Table 1 lists the molar extinction coefficients for the various compounds and also compares our values with previous ones. We conclude that the extinction coefficients of Hwa *et al*.[4] for the hexa-1,3,5-trienes are too high.

[4] Hwa, Sims, and de Benneville, *J. Amer. Chem. Soc.*, 1960, **82**, 2537.
[5] Lippincott and Kinney, *J. Amer. Chem. Soc.*, 1962, **84**, 3641.
[6] Marvel and Hartzell, *J. Amer. Chem. Soc.*, 1959, **81**, 448.
[7] Djerassi, *Chem. Rev.*, 1948, **43**, 293.
[8] Alder and von Brackel, *Annalen*, 1957, **608**, 195.

The percentage conversion of hexa-1,*cis*-3,5-triene into cyclohexa-1,3-diene was calculated from the optical density of a 2,2,4-trimethylpentane solution of the product. Beer's law holds over the concentration range used (1·3—2·5 × $10^{-5}$ mole/l.). Ultraviolet spectra were recorded on a Unicam S.P. 500 spectrophotometer, capable of reproduction to within ±0·2%, with matched 1·0 cm. silica cells.

*Procedure.*—Pure hexa-1,*cis*-3,5-triene was degassed several times and its vapour then allowed to fill a thermostatted vessel to a measured pressure. The reaction vessels, previously evacuated to $10^{-5}$ mm. were filled from this vessel. Pressures in the reaction vessels were calculated from volumes and temperatures. A reaction pressure of 60—80 mm. was used for most experiments. Higher pressures, up to 300 mm., were obtained by using the heated Toepler pump. After reaction, the entire content of each reaction vessel was frozen by liquid nitrogen first into the wide-bore traps and then into the small ampoules. Solutions for analysis were made by breaking the ampoules under 2,2,4-trimethylpentane.

## RESULTS

*Products of Reaction.*—Hexa-1,*cis*-3,5-triene vapour was heated for 2 hr. at 192°. The i.r. and u.v. spectra of the product were identical to those of cyclohexa-1,3-diene. Microhydrogenation over Adams catalyst gave the theoretical absorption for two double bonds. On reaction with maleic anhydride the product gave an adduct of the correct m. p. (147°). The vapour phase chromatogram showed only one peak of a retention time corresponding to that of cyclohexa-1,3-diene.

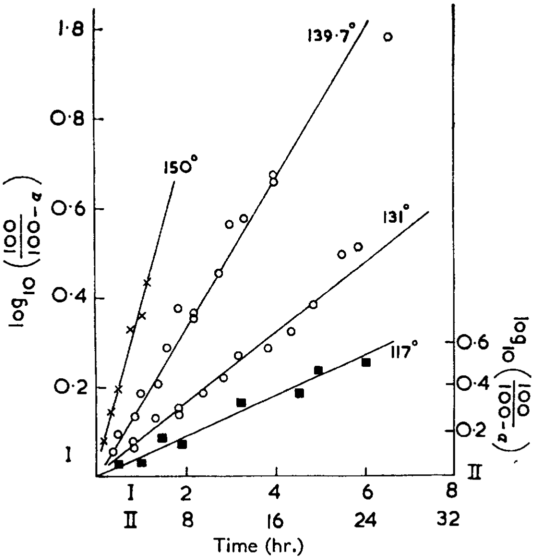

FIG. 1. Rates at various temperatures.
$a$ = % of cyclohexa-1,3-diene.
(I) 131—510°; (II) 117°.

In several experiments it was established that to within 0·1 mm. there was no pressure change during the reaction, and that no gas, uncondensable in liquid air, was formed. No polymer was visible by careful examination of the vessels.

These results exclude dimerisation or polymerisation, which could proceed simultaneously with the isomerisation, and also the formation of hydrogen by dehydrogenation of cyclohexadiene to benzene.

Under the conditions of the thermal isomerisation, cyclohexa-1,3-diene disproportionated to benzene and cyclohexene, as shown by vapour phase chromatography of the product and of cyclohexa-1,3-diene which had been heated under identical conditions. Two small subsidiary peaks could be resolved which were identified as due to benzene and cyclohexene by their retention times and by the addition of these compounds to reinforce the peaks. However, at

161° after 1 hour's reaction time the benzene in the product was less than 1·0%. It was concluded that under the conditions of the kinetic study this side reaction could be disregarded.

*Reaction of Hexa-*1,trans-3,5-*triene*.—This was heated for 2 hr. at 192° in the vapour phase at 60 mm. Hg. No change in the i.r. or u.v. spectra was observed. We conclude that it does not cyclise under these conditions.

*Reaction Rates*.—Figs. 1 and 2 show that, within experimental error, good first-order plots are obtained up to conversions of 80—90%. Runs in the packed vessel, included in Fig. 2, show no significant deviations in rate from those in the empty vessels indicating that the reaction is homogeneous.

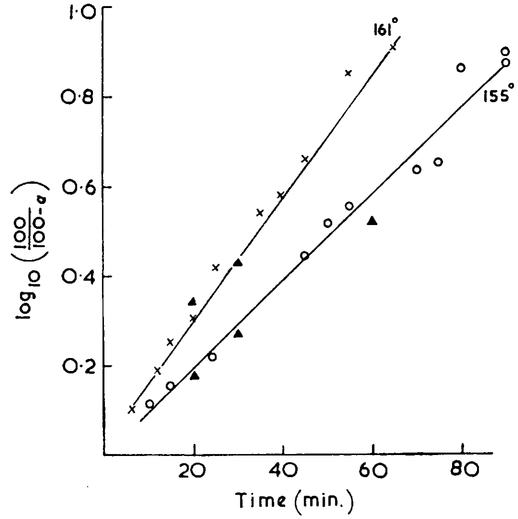

FIG. 2. Rates at 155 and 161°.
▲ Packed vessel.

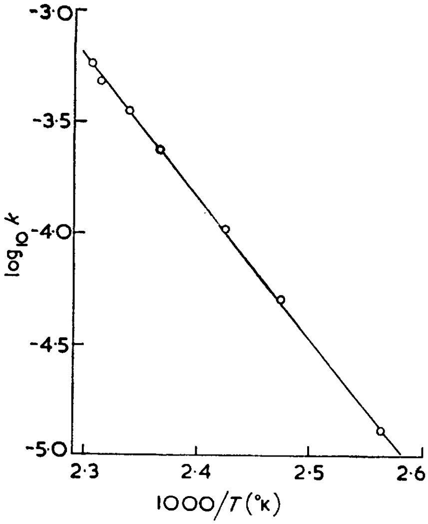

FIG. 3. Temperature dependence of rate.

Table 2 shows the dependence of rate on pressure from 60 to 300 mm. at 159·2° with a fixed reaction time of 20 min. The constancy, within experimental error, of the conversion and of the rate constant further confirms the first-order dependence.

The unimolecular rate constants at various temperatures (Table 3) lead to a good Arrhenius plot (Fig. 3), whose straight line, obtained by a least-squares treatment, gives

$$k = (7{\cdot}15 \pm 5{\cdot}2) \times 10^{11} \exp -(29{\cdot}900 \pm 500)/\boldsymbol{RT} \text{ sec.}^{-1}$$

TABLE 2.

Pressure dependence of rate at 159·2°; time 20 min.

| Pressure (mm. Hg) | $10^{-3}\varepsilon$ at 256 m$\mu$ | Cyclo-hexadiene (%) | $10^4k$ (sec.$^{-1}$) | Pressure (mm. Hg) | $10^{-3}\varepsilon$ at 256 m$\mu$ | Cyclo-hexadiene (%) | $10^4k$ (sec.$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 60 | 21·75 | 43·2 | 4·82 | 200 | 21·80 | 43·0 | 4·68 |
| 100 | 21·80 | 43·0 | 4·68 | 300 | 20·80 | 46·2 | 5·17 |
| 180 | 21·20 | 45·0 | 4·97 | 300 | 21·20 | 45·0 | 4·97 |
| 200 | 22·00 | 42·4 | 4·59 | | | | |

TABLE 3.

Rate constants at various temperatures.

| Temp. .................. | 117·1° | 131·4 | 139·7 | 150·0 | 155·2 | 159·2 | 161·1 |
|---|---|---|---|---|---|---|---|
| $10^5k$ (sec.$^{-1}$)........... | 1·33 | 5·12 | 10·6 | 24·1 | 36·2 | 48·0 | 58·6 |

## DISCUSSION

If one considers the mechanism of the cyclisation in analogy to the general mechanism of diene associations,[9] the two alternative configurations suggested for the transition state of diene associations find their counterparts for the triene cyclisation as in Fig. 4; a linear complex stabilised by delocalisation of electrons (*a*), or a cyclic complex (*b*) which resembles the product (cyclohexadiene) to be formed.

In (*a*) the reaction proceeds in two steps, the slow, rate-determining one being the formation of the complex which subsequently cyclises rapidly. In (*b*) the reaction proceeds in one step, the cyclisation itself being rate-determining.

That hexa-1,*trans*-3,5-triene did not cyclise excludes a linear complex of the extreme diradical form. The *trans*-, unlike the *cis*-compound, cannot form a six-membered ring by rotation around single bonds only. It also excludes the free radical with free or slightly hindered rotation around bond (3,4) as the transition complex, but such a complex with substantially hindered rotation around this bond may still be possible.

Calculations using the standard treatment of the transition-state theory confirm this conclusion and show that the alternative cyclic complex agrees to a satisfactory degree with the experimental results. These calculations were carried out in close analogy to previous ones for the diene associations of ethylene and butadiene, and for the dimerisation of butadiene to cyclohexene and vinylcyclohexene, respectively.[9,10] Very similar reaction centres are involved in these cases.

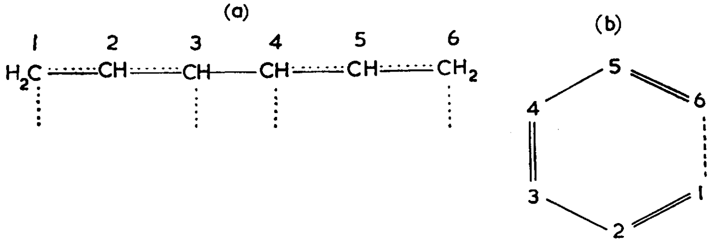

FIG. 4. Transition configuration for cyclisation of hexatriene.

The molecular moments of inertia required for the calculation of the rotational partition functions were obtained from molecular models. The conjugated bond distances were taken as (C=C) = 1·37 and (C–C) = 1·47 Å. The (C–H) distances were taken as 1·06 Å, and for simplification a C–C=C and a H–C=C bond angle of 120° was generally adopted. The moments of inertia so derived are given in Table 4 which includes the moments of inertia for internal rotations and torsional vibrations. Their assignment is indicated in Table 4 and the various axes of rotation are specified in Fig. 5.

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[9] Kistiakowski and Ransom, *J. Chem. Phys.*, 1939, **7**, 725; Wassermann, *J.*, 1942, 612.

[10] Rowley and Steiner, *Discuss. Faraday Soc.*, 1951, **10**, 198.

TABLE 4.

Moments of inertia (g. cm.$^2$ × $10^{40}$).

| | $I_{xx}$ | $I_{yy}$ | $I_{zz}$ |
|---|---|---|---|
| Hexa-1,*cis*-3,5-triene configuration (*a*) (See Fig. 5) | 69 | 486 | 554 |
| ,, ,, (*c*) (See Fig. 5) | 140 | 161 | 298 |
| Mean | 105 | 324 | 426 |
| Cyclohexa-1,3-diene | 144 | 140 | 284 |

| Internal rotations | Reduced moments of inertia |
|---|---|
| Rotation around bonds (2,3) and (4,5) in hexa-1,*cis*-3,5-triene | 26·5 |
| Mean of configuration (*a*), axis (*aa'*) and (*b*), axis (*bb'*) (see Fig. 5) | |
| Torsional vibrations around bonds (2,3) and (4,5) in linear transition complex | |
| Torsional vibration around bond (3,4) in hexa-1,*cis*-3,5-triene | 35 |
| Rotation around bond (3,4) in linear transition complex | |

The symmetry number for all rotational partition functions involved is two and equally the number of equivalent positions for all internal rotations and torsional vibrations The two internal rotations in *cis*-hexatriene should be hindered by a restricting potential, which was taken as 6 kcal./mole for each of the two rotational modes, slightly higher than the equivalent restricting potential in butadiene of 5 kcal.[11] The linear free-radical complex comprises an internal rotation around 4,5-bond (see Fig. 4), which was taken either as a free rotation or alternatively as a hindered one with a restricting potential of 6 kcal./mole.

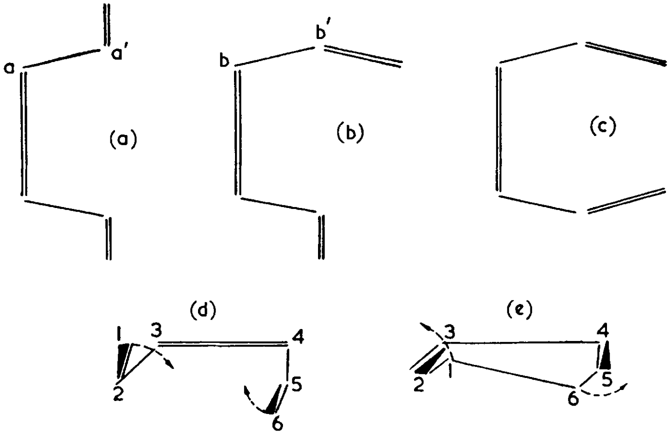

FIG. 5. Configuration of hexa-1,*cis*-3,5-triene (a), (b), (c); transition state for cyclisation (d), and cyclohexadiene (e).

For the calculation of the vibrational partition functions the average vibrational frequencies for hydrocarbons as suggested by Pitzer were used.[12] The frequencies of the transition complexes have been discussed in detail previously.[9,10] For the cyclic complex two alternative values (320 and 190 cm.$^{-1}$) for the C–C–C and C–C=C bending frequencies of bonds associated with bonds to be formed or to be broken were adopted, as discussed elsewhere.[10] The only frequencies not discussed previously were those for the torsional oscillation of the *cis*-triene around the 1,2-, 5,6-, and 3,4-bonds. A frequency in the Raman spectrum of hexatriene at 750 cm.$^{-1}$, assigned by Lippincott [13] to the torsional vibration of the vinyl group [1,2- and 5,6-bonds], was adopted here. This frequency is considerably higher than the corresponding ones in propylene and butadiene owing to the greater restraining potential in hexatriene caused by the increased resonance energy

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[11] Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66; Aston, Szass, Woolley, and Brickwedde, *J. Chem. Phys.*, 1946, **14**, 67.

[12] Pitzer, *J. Chem. Phys.*, 1937, **5**, 469.

[13] Lippincott, White, and Sibilia, *J. Amer. Chem. Soc.*, 1958, **80**, 2926.

Equally the torsional vibration around the centre bond of hexatriene will be more restrained than the corresponding one in but-2-ene but the larger reduced mass slightly over-compensates for this effect, resulting in a shift from 270 cm.$^{-1}$ in but-2-ene to 240 cm.$^{-1}$ in hexatriene. The torsional vibration of the linear transition complex around the 1,2-, 5,6-, and 2,3-, 4,5-bonds, respectively, have also been discussed previously.

Table 5 lists all frequencies used and their magnitudes. The results of this calculation for a temperature of 425°K are in Table 6. The linear complex with free rotation around the 3,4-bond (see Fig. 4) leads to a frequency factor about 60 times too high. This factor is reduced to 15 by assuming a restraining potential of 6 kcal./mole around the bond. However, much better agreement with the experimental frequency factor is obtained for the cyclic complex, the frequency factor for which was calculated assuming average C–C–C frequencies of 320 cm.$^{-1}$ throughout, as well as for the alternative case of a reduced value of 190 cm.$^{-1}$ for those C–C–C frequencies associated with the bond formed in the reaction.

TABLE 5.

Vibration frequencies.

| Mode of vibration | Frequency (cm.$^{-1}$) | Number of modes in: Hexa-1,*cis*-3,5-triene | Cyclic complex | Linear complex |
|---|---|---|---|---|
| 1. C–H stretch | 3000 | 8 | 8 | 8 |
| 2. H–C–H bend | 1440 | 2 | 2 | 2 |
| 3. H–C–C bend in $-\mathrm{C{=}C}<^{\mathrm{H}}_{\mathrm{H}}$ | 950 | 4 | 6 | 4 |
| $\mathrm{C{=}C}<^{\mathrm{H}}_{\mathrm{C}}$ | | 8 | 8 | 8 |
| 4. C–C stretch | 1000 | 2 | 3 | — |
| 5. C=C | 1600 | 3 | 2 | — |
| 6. C ⩦ C | 1335 | — | — | 4 |
| 7. C–C=C bend | 320 | 4 | — | — |
| C–C ⩦ C bend | | — | — | 2 |
| C ⩦ C ⩦ C bend | | — | 4 | 2 |
| C–C --- C bend | 190 | — | 2 | — |
| 8. C=C tors. | 750 | 2 | — | — |
| C=C ,, | 240 | 1 | — | — |
| 9. C ⩦ C tors. | 407 | — | — | 2 |
| C ⩦ C ,, | 190 | — | — | 2 |

TABLE 6.

Frequency factors for triene cyclisation at 425°K.

| | | *A* (sec.$^{-1}$) |
|---|---|---|
| Experimental value | | $7{\cdot}15 \times 10^{11}$ |
| Cyclic transition state | normal bending frequencies | $4{\cdot}27 \times 10^{11}$ |
| | modified bending frequencies | $8{\cdot}31 \times 10^{11}$ |
| Linear transition state | free rotation | $4{\cdot}14 \times 10^{13}$ |
| | hindered rotation | $1{\cdot}10 \times 10^{13}$ |

Thus our evidence favours a cyclic transition state. This agrees with the conclusions of a recent critical survey of a large number of experimental results on diene reactions.[14]

However, consideration of the activation energy of the cyclisation, and particularly a comparison of the activation energy with that of the related diene associations of ethylene and butadiene,[10] and of the dimerisation of butadiene,[9] clearly shows that the model of a cyclic transition state requires modification. The activation energy of the triene cyclisation of 30 kcal./mole is higher than that of the ethylene–butadiene association (25 kcal./mole) * and that of the dimerisation of butadiene (23 kcal./mole). If, as is generally assumed, the cyclic transition complex in the two last reactions is symmetrical with respect to the

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* The value measured of 27 kcal./mole at 900°K should be reduced to 25 kcal./mole when extrapolated to the temperature range of the present experiments of 400°K.[10]

[14] Berson and Remanick, *J. Amer. Chem. Soc.*, 1961, **83**, 4951.

four carbon atoms forming the two new bonds simultaneously (Fig. 6*b*), then we have to compare the interaction of four reaction centres (=$CH_2$ groups), in the association reaction, with only two in the triene cyclisation. The activation energy in these reactions is determined largely by the repulsion of the reaction centres when they approach each other to form the transition configuration. Since four centres are involved in the association, but two in the cyclisation, the activation energy of the former should be appreciably the higher. In fact the cyclisation has the somewhat higher activation energy.

It had been recognised by Evans and Warhurst [15] that in diene associations a symmetrical approach of the dienophil to the diene involves a very large repulsion between the four reaction centres. They tried to overcome the difficulty by introducing a planar and completely symmetrical transition complex with complete delocalisation of the $\pi$ electrons involved. The calculated gain in resonance energy very materially reduced the repulsion which has to be overcome in forming the complex. However, steric considerations rule out such a planar complex.[16]

The following alternative model is suggested to overcome this difficulty (Fig. 6*c*.) The symmetrical, planar complex is replaced by an asymmetrical, non-planar one. Whilst in this complex carbon atoms 1 and 6 approach each other closely enough for reaction to occur, centres 4 and 5 remain at a distance at which repulsion is still small. Once a bond between carbon atoms 1 and 6 begin to form the energy so released can overcome the repulsion between atoms 4 and 5. We assume that this energy can be transferred sufficiently rapidly for the reaction to be completed without intermolecular dissipation of energy.

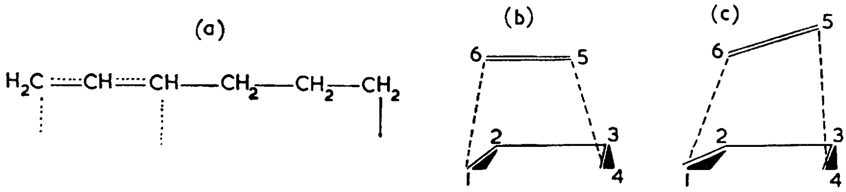

FIG. 6. Transition configurations for butadiene–ethylene association.

A very similar model for the transition configuration of diene reactions has been suggested by Woodward and Katz.[17] The arguments for this model were shown not to be conclusive [14] but our considerations based on the energetics of diene reactions appear to lead to a nearly identical model. To investigate these conditions more closely we calculated approximately the activation energies associated with the various transition configurations, using the semi-empirical method of intersecting potential-energy surfaces of Evans and Polanyi.[18] The lowest point of the line of intersection of the two surfaces gives an upper limit for the activation energy. The difference of this upper limit and the true activation energy is determined by the resonance energy associated with the transition configuration and the approximation involved in this treatment depends, *inter alia*, on the magnitude of this quantity. The cyclisation of *cis*-hexatriene and the association of ethylene and butadiene were examined in this way.

It is possible in these cases, after taking into account all interaction energies involved, to represent the reaction path in a two-dimensional diagram with the interaction energy and the critical C–C distance between two reaction centres as the co-ordinates. For the attraction part of the reaction path C–C Morse potentials, suitably adjusted where necessary, were used. The molecular parameters are in Table 7, together with those for the Morse potential for the C–H bond and C=C double bond, which are also required. The bond dissociation energy of the C–C bond of 75 kcal./mole adopted here is somewhat lower than

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[15] Evans and Warhurst, *Trans. Faraday Soc.*, 1938, **34**, 614; Evans, *ibid.*, 1939, **35**, 824.
[16] Wassermann, *J.*, 1950, 2205.
[17] Woodward and Katz, *Tetrahedron*, 1959, **5**, 70.
[18] Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11.

TABLE 7.

Parameters of Morse function.

$$E = D_0[e^{-2a(r - r_0)} - 2e^{-a(r - r_0)}]$$

| Bond | $D_0$ (kcal./mole) | $r_0$ (Å) | $a$ (Å$^{-1}$) |
|---|---|---|---|
| C–C ............................ | 75 | 1·54 | 1·82 |
| C=C ............................ | 129 | 1·34 | 2·47 |
| C–H ............................ | 93 | 1·06 | 1·94 |

the one found in open-chain compounds but as shown later this value agrees better with thermochemical data for the reactions involved.

The repulsion part of the reaction path which is determined primarily by the repulsion potentials between the non-bonded atoms of the approaching reaction centres, is much less certain. In the absence of a relation with better theoretical foundation we had to rely, as the originators of this method did, on the formula of perfect pairing (1),[15,18,19]

$$E_R = -\sum_i Q_i + \tfrac{1}{2}\sum_i S_i = \alpha\sum_i E_i + \tfrac{1}{2}\sum(1 - \alpha)E_i \tag{1}$$

where $E_R$ refers to the total repulsion energy between two reaction centres, $E_i$ to the total interaction energy between a non-bonded pair, $Q_i$ and $S_i$ are the Coulombic part and the interchange part of this pair potential, and $\alpha$ is the fraction of the total pair potential which is Coulombic. As is common when applying this method a fixed value of 0·15 was taken for $\alpha$, which leads to

$$E_R = 0{\cdot}275 \sum_i E_i$$

Values for the total interaction energy $E_i$ were taken from Morse potentials, the potentials of the carbon–carbon double bond representing the interaction of both the $\sigma$ and $\pi$ electrons forming this bond.

It was found that only interactions of the non-bonded atoms of neighbouring reaction centres contribute significantly to the total repulsion potential. All others, therefore, were neglected. Moreover repulsions between non bonded H–H pairs, even of neighbouring centres, are small enough to be disregarded. The mechanism assumed for the triene cyclisation is illustrated in Fig. 5*d*.

Carbon atoms 1 and 6 (reaction centres) move towards each other by rotation of the 1,2 and 5,6 double bonds, respectively, around the axis represented by the 2,3 and 4,5 single bonds. The reaction co-ordinate can then be represented by the single distance between atoms 1 and 6. The calculation of the associated interaction energy has been discussed already and will be dealt with further below. This part of the reaction path represents the repulsion curve. From the cyclohexadiene side the transition configuration is attained by the movements of atoms 1 and 6 away from each other (Fig. 5*e*), but in this case the bonds around which atoms 1 and 6 have to be rotated, *i.e.*, 2,3 and 4,5 are double bonds. The energy of torsion around these bonds must, therefore, be added to the energy of stretching the 1,6 C–C bond. The sum representing the total energy can then be related to the single 1,6 C–C distance as the only co-ordinate. This part of the reaction path corresponds to the attraction curve. The energy of torsion around the 2,3- and 4,5-bond was calculated by assuming the force constant to be identical with that for the torsional vibration of ethylene ($7{\cdot}00 \times 10^{-12}$ dyne.-cm.) and the torsional movement to be harmonic.

The distances of the interacting atoms at various stages of the reaction were obtained by geometrical construction. For illustration the diagram representing the triene cyclisation is shown in Fig. 7, which gives the planar and end-on views, respectively, of the molecular movement leading to cyclisation. By rotation around the 2,3-bond as axis carbon atom 1 travels from the initial state to the transition configuration along path $P_1$—$P_1'$, the two hydrogen atoms linked to carbon atom 1 along $Q_1$—$Q_1'$ and $R_1$—$R_1'$, respectively. By rotation around $C_{(4)}$–$C_{(5)}$, carbon atom 6 moves along $P_6$–$P_6'$ and the

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[19] Coulson, " Valence," Oxford University Press, 1961, pp. 184, 192.

hydrogen atoms bonded to it along $Q_6$—$Q_6'$ and $R_6$—$R_6'$. The transition complex is located at $C_1$, $H_1$, $H_1'$, and $C_6$, $H_6$, $H_6'$.

From this diagram all required distances between interacting atom pairs can be obtained and the resulting interaction energies calculated in the manner described.

The data for the opening of the cyclohexadiene ring were obtained from a similar diagram including the angles for the torsional movement around the double bonds. The initial state of cyclohexadiene was assumed to be non-planar, with angles between bonds 2,1 and 5,6, respectively, and the plane of the 2,3- and 4,5-bonds of 10°. The potential energy calculated for the various configurations along the reaction path is plotted in Fig. 8 against the distance between carbon atoms 1 and 6 for the critical range of 1·8—2·8 Å. Curve $A_1$ represents the repulsion part and $R_1$ the attraction part of the reaction path. The difference in energy of the initial and final states determines the relative zero position of the two curves. In the triene cyclisation one double bond is opened (54 kcal.) and one single bond is formed (—75 kcal.), at the same time the resonance energy of the triene is lost (11 kcal.) [20] and that of the cyclohexadiene (—2 kcal.) is gained. The total energy change therefore equals —12 kcal.

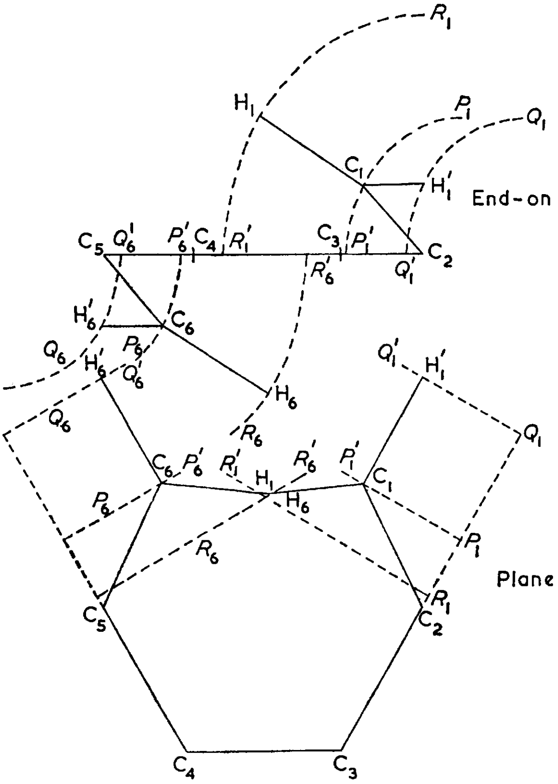

FIG. 7. Cyclisation of hexatriene.

This exothermic energy term readily explains the completeness of the cyclisation reaction in the temperature range studied, the favourable energy term completely outweighing the entropy loss on cyclisation.

The energy level of the crossing point of curves $A_1$ and $R_1$ in Fig. 8 lies 30 kcal. above that of the initial configuration. To this energy difference has to be added the energy necessary to convert the triene from the most stable extended form (Fig. 5*a*) to the initial state of the cyclisation process (Fig. 5*d*).

[20] Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; Coulson, *ibid.*, 1938, *A*, **164**, 383.

The energy differences associated with these changes were taken from the known case of butadiene.[11] Accordingly configuration (*b*) (Fig. 5) was assumed to be less stable than (*a*) by 2 kcal. and configuration (*d*), which can be taken as the initial state of the triene cyclisation, to be less stable than configuration (*b*) by 5 kcal. A total of 7 kcal. therefore would have to be added to the energy difference at the crossing point of 30 kcal. However, the energy difference between configurations (*b*) and (*d*) of Fig. 5 is mainly due to the loss of resonance energy of the triene system when the 5,6-bond is moved out of the plane of the 1,2-, 2,3-, 3,4-, and 4,5-bonds. Some or most of this energy difference has been accounted for already in the adjustment of the energy levels of initial and final state when the loss of resonance energy in going from the triene to the diene configuration had been taken into account. The final activation energy calculated for the triene cyclisation lies therefore between 32 and 37 kcal., compared with the experimental activation energy of 30 kcal. In view of the very approximate nature of this calculation and the fact that the value obtained is an upper limit, the agreement seems very reasonable.

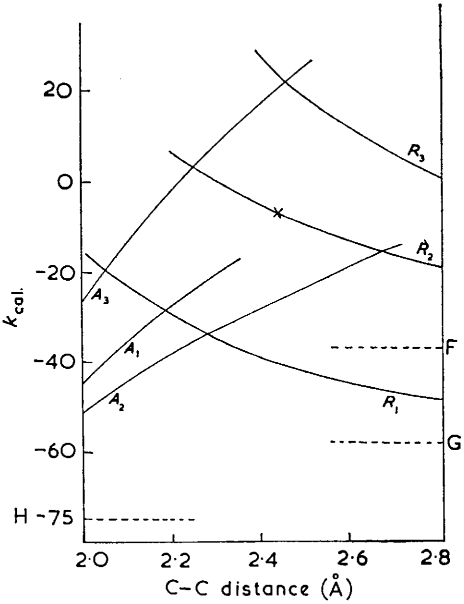

FIG. 8. Attraction and repulsion potentials for cyclisation of hexatriene and association of ethylene and butadiene.

(F) Zero for butadiene and ethylene; (G) Zero for hexatriene; (H) Zero cyclohexadiene and cyclohexene.

The activation energy of the association of butadiene and ethylene to form cyclohexene was calculated similarly to that of the triene cyclisation. The asymmetric approach of the ethylene to the butadiene molecule, described previously (Fig. 6*c*) was adopted as a basis. The various interatomic distances and, hence, the repulsion potentials were obtained from a diagram similar to Fig. 7. Many variations of the approach of the ethylene to the butadience molecule are possible. The smallest repulsion is incurred by an approach of the ethylene from above the plane of the butadiene molecule. This can be further reduced by rotation of the ethylene around the C=C bond as axis, which for a given distance between carbon atoms 1 and 6 increases all critical C–H distances and thus decreases repulsion. The transition configuration found in this way is that indicated in Fig. 6*c*.

The path of the reverse reaction of the dissociation of cyclohexene into ethylene and butadiene is determined by the stretching of the 4,5 C–C bond which to this approximation can be represented by a simple C–C Morse potential.

The attraction and repulsion curves for the cyclohexene dissociation and the ethylene–butadiene association are represented in Fig. 8 by curves $A_2$ and $R_2$, respectively. The relative position of the two curves is determined by the energy difference of opening two double bonds (2 × 54 kcal.), the formation of two single bonds (−2 × 75 kcal.), and the loss of resonance energy of the butadiene molecule (4 kcal.) which leads to a value of −38 kcal. for the energy change. By the choice of 75 kcal. for the C–C bond dissociation energy in cyclohexene close agreement is achieved with the value of −39 kcal. for this energy change as derived from thermal data.* This is why this low value, which may be due to strain in the cyclic structures involved, is adopted.

The energy level of the crossing point of the attraction and repulsion curves lies 22 kcal. above that of the initial state. To this quantity has to be added the energy difference between *trans*- and *cis*-butadiene (2 kcal.) since the conversion from the more stable *trans*- to the *cis*-isomer must precede the reaction with ethylene. The total of 24 kcal. represents the activation energy of the association reaction, if, as has been assumed, no energy is expended to overcome the repulsion of the reaction centres 3 and 4 during the approach of atoms 1 and 6.

This total of 24 kcal. is smaller, though only slightly so, than the experimental value of 25 kcal., whereas the calculated value, which represents an upper limit, should be higher. A more serious objection is the location of the crossing point at a distance of 2·68 Å. This seems to be a large distance for a perturbation of the electronic systems of the two reactants of sufficient intensity to induce frequent crossings from the repulsion to the attraction curve of the reaction path. The crossing point is shifted to a smaller C–C distance and at the same time to a higher energy level if a steeper C–C attraction curve is adopted. Such an increase in the slope would result if the energy for distorting the C–C–C bond angles, associated with the dissociating bond of cyclohexene, were taken into account, but this effect alone is comparatively small and insufficient to change the attraction curve appreciably. A factor which may be more important is a stretching of the 1,6-bond in addition to that of 4,5-bond, which may be necessary for dissociation to occur. Assuming that due to these combined factors an additional 20 kcal. is expended in the dissociation reaction this would shift the crossing point inward to a C–C distance of 2·43 Å and simultaneously upward to an energy level of 30 kcal. above the initial configuration as indicated on Fig. 8 (point $X$). This is a more reasonable distance for the crossing from repulsion to attraction curve to occur; at the same time the activation energy associated with this mode of reaction is still compatible with the experimental one.

The activation energy of the association reaction under the assumption of a symmetrical approach of the two reactants is estimated by doubling the repulsion and attraction potentials between one pair of reaction centres. The resulting curves, $A_3$ and $R_3$ of Fig. 8, lead to an activation energy of 59 kcal., when correction is made for the *trans*, *cis*-isomerisation of butadiene. Thus the calculated activation energy assuming a symmetrical transition configuration is more than double the experimental value. The only factor which could reduce the discrepancy significantly would be a large resonance energy associated with the transition configuration. However, as discussed previously, this is excluded on stereochemical grounds.

On the other hand, reasonable agreement is obtained between the experimental activation energy and the calculated one, the asymmetrical transition complex being assumed. The agreement is similar to that for the cyclisation of hexatriene, and holds not only for the absolute values of the two activation energies, but also for their relative magnitude. The higher activation energy of the cyclisation reaction appears to be due to the energy required to distort the double bonds of cyclohexadiene in the dissociation step and to the smaller exothermicity of the reaction. Both factors lead to a relative position of the

* This energy change was calculated from the heats of formation of ethylene [21a] and butadiene,[11] the heat of combustion of cyclohexane [21a] and the heat of hydrogenation of cyclohexene.[21b] Values at 298°K were equated to those at 425°K and $\Delta E_{425}{}^{\circ} = (\Delta H_{425}{}^{\circ} - 850)$ cal. mole$^{-1}$.

[21] (*a*) Selected Values of Properties of Hydrocarbons, U.S. National Bureau of Standards, Nov. 1947; (*b*) Kistiakowski, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**, 146.

attraction and repulsion part of the reaction path which is less favourable than that for the association reaction.

In view of the crudity of the " naïve " semi-empirical approach on which the present calculations are based the agreement is, in fact, surprising. If some significance is accorded to these calculations because of this agreement then *a fortiori* the underlying reaction mechanism and the associated transition configurations must be attributed a similar degree of validity.

These calculations may also explain the results of experiments by Walling and his collaborators [22] on the rate of diene associations at high pressures. The particular reactions investigated, though different from the association of butadiene and ethylene, are sufficiently similar to be discussed. Because of the reduction in volume which occurs in these associations, the reaction rate should be greatly accelerated by pressure. Qualitatively this effect is found but quantitatively the acceleration is insufficient to be compatible with a volume contraction, on forming the transition configuration, which corresponds approximately to that of the final product. This result was brought forward as evidence against a cyclic and in favour of an open-chain transition configuration, on the argument that the configuration of the cyclic transition state and that of the final product should be very similar, whereas this is not so for the linear complex. Our results may explain the discrepancy; first because the asymmetric complex assumed here is likely to occupy a larger volume than the symmetrical; secondly because the calculations show that an appreciable extension of the critical bonds is necessary in forming the transition configuration and before reaction can occur. Both factors would lead to a transition configuration of larger volume than that of the association product.

The award of a D.S.I.R. studentship to K. E. L. is gratefully acknowledged.

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[*Received, August 2nd*, 1963.]

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[22] Walling and Peisach, *J. Amer. Chem. Soc.*, 1958, **80**, 5819; Walling and Schugar, *ibid.*, 1963, **85**, 607; Walling and Tanner, *ibid.*, 1963, **85**, 612.