Unimolecular Isomerisation of Hexa-1,*trans*-3,5-triene and Symmetry-forbidden Pyrolysis of Cyclohexa-1,3-diene

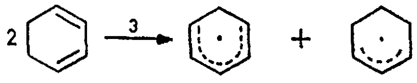
By S. W. Orchard and B. A. Thrush*

(*Department of Physical Chemistry, Lensfield Road, Cambridge* CB2 1EP)

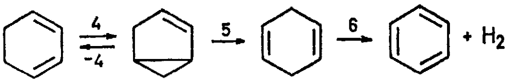
Summary Arrhenius parameters are reported for the thermal isomerisation of hexa-1,*trans*-3,5-triene to the *cis*-compound and for the unimolecular decomposition of cyclohexa-1,3-diene to benzene and hydrogen which is symmetry-forbidden as a direct concerted process and proceeds *via* cyclohexa-1,4-diene.

We have studied the gas-phase pyrolysis of hexa-1,*trans*-3,5-triene in an aged 10 l Pyrex bulb at 587·9 and 639·7 K. Reaction apparently occurs *via* hexa-1,*cis*-3,5-triene to yield cyclohexa-1,3-diene which is not decomposed at the reactant pressures used (1—20 mTorr). The rate coefficient k_1 was constant over three half-lives and showed the low pressure fall-off characteristic of unimolecular reactions. 20 Torr of nitrogen restored k_1 to its limiting high-pressure value. Reaction (2) is fast enough[1] to make the reverse geometrical isomerisation negligible. Our Arrhenius expression $k_1 = 10^{12.65 \pm 0.18} \exp(-181{\cdot}3 \pm 2{\cdot}0\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{s^{-1}}$ agrees well with that for corresponding isomerisation of hepta-1,*trans*-3,*trans*-5-triene[2] and a reported activation energy[3] for reaction (1).

At reactant pressures above 1 Torr the pyrolysis of cyclohexa-1,3-diene involves a chain mechanism yielding benzene, cyclohexene, and dimeric products.[4,5] We have studied this reaction at six temperatures between 719 and 824 K using reactant pressures of 4—40 mTorr to minimise the reported bimolecular initiation step [see reaction (3)]. Although there was evidence of a chain reaction at higher reactant pressures, the decomposition of cyclohexa-1,3-diene was first order to at least 70% conversion and the rate constant was independent of reactant pressure below 20 mTorr where it was unaffected up to 10 Torr added propene. Under such conditions no cyclohexene was found, the products being at least 98% benzene and hydrogen. The rate expression in the presence of excess of nitrogen is $k_{3a} = 10^{13.67 \pm 0.28} \exp(-258 \pm 4\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{s^{-1}}$, supporting the sequence of reactions (4), (5), and (6).



The published values [5,6] of k_{-4}, k_5, and k_6 are more than 1000 times k_{3a}. As $k_6 >> k_5$, this mechanism yields $k_{3a} = k_4k_5/(k_{-4} + k_5)$. The ratio $(k_{-4} + k_5)/k_5 = 2{\cdot}51$ and is independent of temperature.[5] Hence $k_4 = 10^{14.07}$ exp $(-258$ kJ mol$^{-1}/RT)$ s^{-1}. For the reverse reaction[5] $k_{-4} = 10^{14.28}$ exp$(-210$ kJ mol$^{-1}/RT)$ s^{-1}. The estimated enthalpy difference between the two compounds is 49 kJ mol^{-1} [7,8] and the estimated entropy change at 800 K gives $A_{-4}/A_4 \simeq 4$ although the measured ratio will be lower if reactions (−4) and (5) proceed *via* a common (biradical) intermediate which rapidly reforms bicyclo[3,1,0]hex-2-ene.[8] Their agreement within experimental error with the measured Arrhenius parameters shows clearly that the thermal unimolecular conversion of cyclohexa-1,3-diene into benzene and hydrogen occurs *via* cyclohexa-1,4-diene: a small steady-state concentration of bicyclo[3,1,0]hex-2-ene is also present, but some direct 1,3 to 1,4 isomerisation *via* a biradical intermediate[8] is not excluded.



There is no evidence of the direct concerted loss of *cis*-hydrogens which is forbidden by the Woodward–Hoffmann rules.[9] The heats of formation of the 1,3- and 1,4- cyclohexadienes[7] differ by less than 2 kJ mol^{-1}, and for the latter the symmetry-allowed concerted formation of benzene and hydrogen has $k_6 = 10^{12.2}$ exp$(-181$ kJ mol$^{-1}/RT)$ s^{-1},[5,6] a path 77 kJ mol^{-1} lower than that by which cyclohexa-1,3-diene avoids violation of the Woodward–Hoffmann rules.

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