# 63. *The Thermal Isomerisation of Quadricyclene (Quadricyclo-*$[2,2,1,0^{2,6},0^{3,5}]$*heptane). Part I. The Gas-phase Reaction.*

By H. M. Frey.

In the range 150—190°, quadricyclene isomerises to bicyclo[2,2,1]-hepta-2,5-diene. In a Pyrex reaction vessel the reaction is homogeneous, of the first order, and independent of pressure (1—18 mm.). Addition of propene or a large excess of nitrogen does not affect the rate constants. It is almost certainly a unimolecular transformation. Comparison of its energy of activation with that of the decomposition of *cis*-1,2-dimethylcyclobutane indicates that quadricyclene has about 27 kcal. mole$^{-1}$ more strain energy than the cyclobutane.

THE observation[1] that quadricyclene (I) isomerises to the bicycloheptadiene (II) at ~140° implies that the former has considerably more strain energy than the already strained diene. The isomerisation is formally the same as that of cyclobutanes[2,3] to olefins, but the latter occur at >400°. It was expected that this valency-bond isomerisation would be unimolecular, as with cyclobutanes, so that a kinetic investigation would allow the strain energy of quadricyclene to be calculated. The possibility that the reaction might be suitable for investigation both in the gas and the liquid phase gave added impetus to the work.

## EXPERIMENTAL

Quadricyclene (quadricyclo$[2,2,1,0^{2,6},0^{3,5}]$heptane) was prepared by the photosensitised isomerisation of bicyclo[2,2,1]hepta-3,5-diene.[1] A solution of the diene (25 g.) and acetophenone (5 g.) in isopentane (200 ml.) was irradiated by a 500-w medium-pressure mercury lamp. The lamp was surrounded by a water-cooled jacket, and the solution was contained in the annulus between this jacket and a cylindrical vessel, the latter being provided with a reflux condenser. Virtually all the radiation of the lamp shorter than 3200 Å was absorbed. Irradiation was continued until all the bicycloheptadiene had disappeared. The solution was then fractionally distilled and the fraction boiling at 105—110° was collected. Analysis showed this to contain 98% of quadricyclene with 2% of bicycloheptadiene. When kept for several months the quadricyclene slowly decomposed with formation of a non-volatile white solid polymer. In the course of the work, the percentage of bicyclohexadiene in the starting material rose from 2 to 5%.

*Apparatus.*—A conventional high-vacuum "static" system was employed. Greaseless diaphragm valves were used to minimise absorption. Most runs were carried out in a spherical, Pyrex, reaction vessel of ~150 ml. A few runs were in a cylindrical Pyrex vessel of almost the same volume, packed with Pyrex tubes, with a surface : volume ratio 10 times larger. The reaction vessels were mounted vertically in a high-temperature oil-thermostat (Ultra-thermostat type NB.HT). The temperature gradient over the entire reaction vessel was less than 0·05° and while there was a brief cycle of temperature of nearly ±0·1°, the mean temperature could be held indefinitely within ±0·02°. Temperatures were measured with a standardised mercury-in-glass thermometer. Temperatures should, therefore, be reproducible and accurate to better than ±0·15°. By placing a diaphragm valve immediately outside the thermostat-bath the dead space was reduced to 0·2%.

*Analysis.*—Analysis was by gas chromatography on a 5-ft. column packed with Chromosorb P containing 15% w/w of dinonyl phthalate and operated at room temperature. Hydrogen was the flow gas, a Gow Mac 9285 katharometer the detector, and signals from the latter were measured on a 1 mv recorder and integrated electronically. The inlet system of the chromatograph employed a six-way, stainless-steel stopcock of the type described by Pratt and Purnell.[4] Runs were analysed in duplicate.

---

[1] Hammond, Turro, and Fischer, *J. Amer. Chem. Soc.*, 1961, **83**, 4674.

[2] Genaux, Kern, and Walters, *J. Amer. Chem. Soc.*, 1953, **75**, 6196.

[3] Das and Walters, *Z. phys. Chem. (Frankfurt)*, 1958, **15**, 22; Wellman and Walters, *J. Amer. Chem. Soc.*, 1957, **79**, 1542.

[4] Pratt and Purnell, *Analyt. Chem.*, 1960, **32**, 1213.

## RESULTS AND DISCUSSION

In the temperature range 150—190°, quadricyclene (I) undergoes a " clean " first-order isomerisation to the bicycloheptadiene (II). At each temperature investigated, at least 10 runs were carried out with the decomposition varying from 10 to 70%. In each case the plot of log (initial quadricyclene minus final quadricyclene) against time gave a good straight line, from which the rate constant (see Table) was calculated by the method of least squares. Initial experiments showed that the rate constants were independent of pressure in the range 1—18 mm. of quadricyclene.


(I) (II)

Rate constants for the isomerisation of quadricyclene (3—4 mm.).

| Temp. | 188·5° | 182·3° | 176·6° | 169·7° | 164·1° | 159·3° | 154·0° |
|---|---|---|---|---|---|---|---|
| $10^4k$ (sec.$^{-1}$) | 8·60 | 5·94 | 3·42 | 1·96 | 1·11 | 0·722 | 0·496 |

Six runs were carried out at 176·6° (all for 30 minutes) in which 3 mm. of quadricyclene was isomerised in the presence of 1—10 mm. of added propene. The mean value of the rate constant obtained in these runs was $3{\cdot}40 \times 10^{-4}$ sec.$^{-1}$. Similarly, with another six runs at the same temperature, nitrogen was added (10—100 mm., with 3 mm. of quadricyclene); the mean value of the rate constant for these runs was $3{\cdot}39 \times 10^{-4}$ sec.$^{-1}$. Finally a series of 10 runs (times 10—45 minutes) was carried out at this temperature in the packed reaction vessel; the points so obtained fell on the same line as those obtained at the same temperature in the unpacked reaction vessel, and yielded the same rate constant. These results with the added gases and the packed reaction vessel indicate that the reaction is entirely homogeneous and is also probably unimolecular.

An Arrhenius plot of the results given in the Table gave a good straight line from which the frequency factor and energy of activation for the reaction were calculated by the method of least squares, whence

$$k = 10^{12\cdot81} \exp(-33{,}510/\boldsymbol{RT}) \text{ sec.}^{-1}.$$

The isomerisation of quadricyclene to bicycloheptadiene is formally similar to that of cyclobutane[2] and alkylcyclobutanes[3,5] to olefins. In both cases the four-membered ring is broken and two double bonds are formed. For cyclobutanes this results in the formation of two molecules, but in the present case the two double bonds have to be retained in the same molecule. A comparison of the Arrhenius parameters obtained in this work with those for the decomposition of *cis*-1,2-dimethylcyclobutane[5] (to yield two molecules of propene), *viz.*, $k = 10^{15\cdot48} \exp(-60{,}400/\boldsymbol{RT})$ sec.$^{-1}$, is instructive. This difference, 26·9 kcal. mole$^{-1}$ is, therefore, identified as the difference in strain energy between quadricyclene and the cyclobutane. The very high value for the frequency factor for the decomposition of the dimethylcyclobutane is not exceptional for this type of reaction, and indeed almost identical values have been obtained for cyclobutane and methylcyclobutane. Such frequency factors result from the large positive entropies of activation associated with processes involving ring opening. For cyclobutanes they imply a transition state where (*a*) the ring is so enlarged that rotation of the various groups is either free or only slightly hindered or (*b*) a tetramethylene biradical is involved.[6] The " normal " value for the frequency factor obtained for the present isomerisation is in sharp contrast with these high values. It is, however, entirely to be expected, since the

---

[5] Gerberich and Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935.

[6] Ellis and Frey, *Trans. Faraday Soc.*, 1963, **59**, 2076.

geometries of both the quadricyclene and the bicycloheptadiene molecule must lead to a relatively rigid transition state in which there can be no " new " free rotations. Indeed, the Arrhenius parameters for this isomerisation are more closely related to those obtained for the isomerisations of cyclobutenes to dienes [7] than to the cyclobutane reactions.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, SOUTHAMPTON.

[*Received, May* 31*st*, 1963.]

---

[7] Cooper and Walters, *J. Amer. Chem. Soc.*, 1958, **80**, 4220; Frey, *Trans. Faraday Soc.*, 1962, **58**, 957.