

# Thermal Isomerization of Cyclobutenes

## Part 17.—1-Ethyl-2-Vinylcyclobutene and 1,2,3-Trimethylcyclobutene

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The gas-phase thermal isomerizations of 1-ethyl-2-vinylcyclobutene and 1,2,3-trimethylcyclobutene have been studied in the temperature ranges 434–465 K and 424–464 K respectively. Both isomerizations are homogeneous and first order, and probably unimolecular. 1-Ethyl-2-vinylcyclobutene yields 2-ethyl-3-vinylbuta-1,3-diene, and the rate constants fit the Arrhenius equation,

$$\log k_1/s^{-1} = 13.729 \pm 0.172 - (149\,390 \pm 1\,480 \text{ J mol}^{-1}/2.303 RT).$$

1,2,3-Trimethylcyclobutene yields trans-2,3-dimethylpenta-1,3-diene as the only product and the rate constants fit the Arrhenius equation

$$\log k_2/s^{-1} = 13.276 \pm 0.142 - (141\,180 \pm 1\,200 \text{ J mol}^{-1}/2.303 RT).$$

These results are consistent with the noted insensitivity of the rates of isomerizations of cyclobutenes to the nature of the substituent, and are in line with the additivity relationships discussed previously.

The thermal isomerization of cyclobutene and a number of its derivatives are good examples of unimolecular reactions.<sup>1</sup> For alkyl derivatives the rate of isomerization is insensitive to the nature of the substituent. The rate is, however, affected by the position of substitution on the cyclobutene ring and an additivity relationship has been proposed which allows the free energy of activation to be predicted in a number of systems.<sup>2</sup> To date, there have been only two detailed studies of 1,2-disubstituted cyclobutenes in the gas phase<sup>3</sup> and the present work was undertaken to see if the additivity relationships fitted such molecules.

## EXPERIMENTAL

1-Ethyl-2-vinylcyclobutene of about 90 % purity, prepared by the base-catalyzed isomerization of 1,2-divinylcyclobutane,<sup>4</sup> was provided by Dr. P. Heimbach. It was purified by gas chromatography on a 7 m by 6 mm column containing 20 % w/w  $\beta\beta'$ -oxydipropionitrile on Chromosorb P. 1-Ethyl-2-vinylcyclobutene was obtained better than 98 % pure, and the impurities present were subsequently shown to be thermally stable and not to interfere in any way with the analysis of reaction mixtures.

3,4-Dimethyl-3-acetyl- $\Delta'$ -pyrazoline was prepared by the reaction of 3-methylpent-3-ene-2-one with diazomethane in dry ether at room temperature. The pyrazoline was photolyzed as a 5 % solution in ether, using a medium-pressure mercury lamp. Photolysis was continued until nitrogen evolution ceased. The ether was removed by distillation and the product mixture fractionally distilled to yield a pure sample of 1,2-dimethyl-1-acetyl-cyclopropane.

The 1,2-dimethyl-1-acetylcyclopropane was converted into its tosyl hydrazone by treatment with methanolic toluene sulphonylhydrazide and the hydrazone decomposed by treatment with sodium methoxide in diglyme at 140°C. 1,2,3-Trimethylcyclobutene was removed from this reaction mixture in a stream of dry nitrogen and collected in a trap cooled to –78°C. The crude product was washed with water and dried and then purified by preparative gas chromatography using  $\beta\beta'$ -oxydipropionitrile as the liquid phase. 1,2,3-Trimethylcyclobutene better than 99 % pure was obtained in this way. Its structure was confirmed by n.m.r. spectroscopy.

## APPARATUS

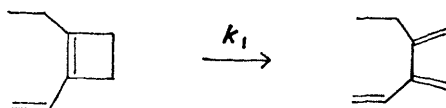
Conventional high-vacuum equipment was employed and all stopcocks were of the greaseless (Viton A diaphragms) type. For the ethylvinylcyclobutene, the reaction vessels were immersed in a high-temperature thermostat using a salt eutectic<sup>5</sup>; in the studies with 1,2,3-trimethylcyclobutene a high temperature oil thermostat was used.<sup>3</sup>

Reaction mixtures were analyzed by gas chromatography and all analyses were carried out at least in duplicate. Chromatographic peaks were integrated either with a ball and disc integrator or electronically. For the trimethylcyclobutene added cyclohexene was used as an internal standard. Products were trapped on elution and identified by n.m.r. spectroscopy.

## RESULTS

## 1-ETHYL-2-VINYLCYCLOBUTENE

The isomerization of 1-ethyl-2-vinylcyclobutene in the temperature range 434–465 K yields 2-ethyl-3-vinylbuta-1,3-diene as the only product



Rate data were obtained at 6 temperatures. At each temperature an average of 10 runs for different reaction times were carried out. In all cases good first-order plots were obtained and the rate constants were calculated from these plots by the method of least squares. The values of the rate constants (rounded off) are shown in table 1.

TABLE 1.—RATE CONSTANTS FOR THE ISOMERIZATION OF 1-ETHYL-2-VINYLCYCLOBUTENE

temp./K	434.2	442.3	449.3	454.7	460.4	465.2	438.8*
$10^4 k_1/\text{s}^{-1}$	0.578	1.19	2.35	3.72	6.10	8.90	0.887

\* packed reaction vessel.

For the majority of runs an initial reactant pressure of  $130 \text{ N m}^{-2}$  (1.0 Torr) was used, but increasing this to  $400 \text{ N m}^{-2}$  had no effect on the measured rate constant. It is clear that even at the lower pressure the isomerization is in its high pressure region. An Arrhenius plot of the data in table 1 fitted the equation,

$$\log k_1/\text{s}^{-1} = 13.729 \pm 0.172 - (149\,390 \pm 1\,480 \text{ J mol}^{-1}/2.303 RT),$$

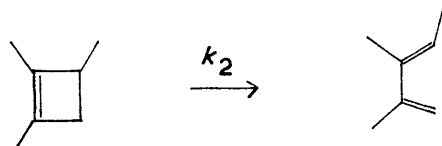
where the error limits are one standard deviation.

Runs were carried out in a packed reaction vessel where the surface-to-volume ratio was 10 times greater than that of the unpacked vessel normally employed. The first run in the packed vessel yielded in addition to 2-ethyl-3-vinylbutadiene a further product (possibly a diethylidene cyclobutane). The relative amount of this other product decreased rapidly in subsequent pyrolyses and after five pyrolyses became negligible. It appears probable that this product arises by a heterogeneous process which takes place on clean Pyrex surfaces, but no longer occurs once the surface has been "aged". After this, the rate of isomerization obtained from studies in the packed vessel fitted exactly on the Arrhenius line obtained for the unpacked vessel.

In two series of runs at different temperatures, rates were determined using *n*-nonane as an internal standard. Rates derived for these experiments were within 1 % of those obtained without the use of an internal standard.

## 1,2,3-TRIMETHYLCYCLOBUTENE

In the temperature range 424–464 K, 1,2,3-trimethylcyclobutene isomerizes to trans-2,3-dimethylpenta-1,3-diene quantitatively.



Runs were carried out at 443.1 K for 18 min using a series of initial pressures in the range 0.6 to 13 kN m<sup>-2</sup>. Within experimental error all these runs showed the same extent of reaction. In subsequent runs initial reactant pressures in the range 1.3–2.6 kN m<sup>-2</sup> were used. Nine series of runs were carried out at various temperatures and in each case good first-order plots were obtained. The rate constants calculated from a least-squares analysis of these plots are shown in table 2. In a further series of runs at 449.1 K, the reaction was investigated in a packed reaction vessel which had a surface-to-volume ratio 14 times that of the unpacked vessel. The rate constant obtained in the packed vessel was identical within experimental error with that calculated from the Arrhenius equation for the unpacked vessel. There can thus be no appreciable surface reaction.

TABLE 2.—RATE CONSTANTS FOR THE ISOMERIZATION OF 1,2,3-TRIMETHYLCYCLOBUTENE

temp./K	424.0	428.3	433.3	438.2	443.6
10 <sup>4</sup> k <sub>2</sub> /s <sup>-1</sup>	0.766	1.17	1.71	2.82	4.53
temp./K	449.1*	453.0	457.3	460.2	463.4
10 <sup>4</sup> k <sub>2</sub> /s <sup>-1</sup>	7.22	10.45	13.7	17.6	23.0

\* packed reaction vessel

The data in table 2 yielded the Arrhenius equation.

$$\log k_2/\text{s}^{-1} = 13.276 \pm 0.142 - (141\,200 \pm 1\,200 \text{ J mol}^{-1}/2.303 RT).$$

## DISCUSSION

The rates of isomerization of variously substituted cyclobutenes appear to be more sensitive to the positions of substitution than on the nature of the substituting group. Thus, for the 1-alkylcyclobutenes all the rates are similar. At 450 K, the free energy of activation of five 1-alkylcyclobutenes fall within the range  $138.8 \pm 0.4 \text{ kJ mol}^{-1}$ . Thus, this substitution raises the free energy of activation by  $4.9 \text{ kJ mol}^{-1}$  compared with cyclobutene itself. For 1,2-dimethylcyclobutene and 1,2-bis(trimethylsiloxy)-cyclobutene the free energies of activation (at 450 K) are respectively 143.3 and 144.3 kJ mol<sup>-1</sup>. For the isomerization of 1-ethyl-2-vinylcyclobutene reported here we obtain  $\Delta G^\ddagger = 142.9 \text{ kJ mol}^{-1}$ . These three values, while not as close as those obtained for the 1-alkyl substituents, do nevertheless illustrate how insensitive the rate of isomerization is to the exact nature of the substituents. The mean value for these three compounds,  $143.7 \text{ kJ mol}^{-1}$  is  $4.9 \text{ kJ mol}^{-1}$  greater than the value for 1-alkyl substituted cyclobutenes. While the exact agreement is undoubtedly fortuitous, it is nevertheless clear that the second substituent on the double bond in cyclobutene produces an incremental effect on the value of  $\Delta G^\ddagger$  closely similar to that of the first.

It is possible to produce a series of additivity values which depend only on the position of substitution on the cyclobutene ring and enable the rate of isomerization of an unstudied cyclobutene to be predicted.<sup>2</sup> On the basis of such values,  $\Delta G^\ddagger$  for 1,2,3-trimethylcyclobutene was estimated to be 138.9 kJ mol<sup>-1</sup>. The value found in the present study is 138.6 kJ mol<sup>-1</sup>, and the agreement is satisfactory. While the additivity values were initially developed to be applied essentially to methyl substituted cyclobutenes, the insensitivity to the value of the substituent of the rates does suggest that these values will apply as well to other alkyl substituents, though there may have to be correction factors for different steric repulsions in some cases.

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<sup>1</sup> W. Cooper and W. D. Walters, *J. Amer. Chem. Soc.*, 1958, **80**, 4220; W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, 1963, **67**, 1328; H. M. Frey, D. C. Hashall and R. F. Skinner, *Trans. Faraday Soc.*, 1965, **61**, 861.

<sup>2</sup> H. M. Frey, B. M. Pope and R. F. Skinner, *Trans. Faraday Soc.*, 1967, **63**, 1166.

<sup>3</sup> H. M. Frey, *Trans. Faraday Soc.*, 1963, **59**, 1619; J. J. Bloomfield, H. M. Frey and J. Metcalfe, in press.

<sup>4</sup> P. Heimbach and R. Schimf, *Angew. Chem. Int. Ed.*, 1969, **8**, 206.

<sup>5</sup> R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 1964, 4184.