# Gas Phase Pyrolysis of Cyclopropene

## Part 1.—Kinetics and Mechanism

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The vapour phase kinetics of pyrolysis of cyclopropene have been studied both by product formation and reactant loss relative to an internal standard in the temperature range 466-516 K. The major product is methylacetylene while the minor one is allene; there is evidence for some material loss under the conditions of these experiments (partial pressures of cyclopropene, $\leqslant 2$ Torr ‡ highly diluted in $N_2$ or $SF_6$). Under conditions of minimal material loss methylacetylene is formed by a homogeneous unimolecular reaction whose rate constant is dependent on total pressure. At $(70\pm2)$ Torr of $SF_6$, which is close to the high pressure limit, the following Arrhenius equation is found

$$\log k/\mathrm{s}^{-1} = (13.09\pm0.04)-(156.1\pm0.4\ \mathrm{kJ\ mol}^{-1})/RT\ln 10.$$

Allene appears to be formed by two pathways, one molecular the other radical in nature. A rate constant for the former has been measured. A unimolecular " fall-off " curve for methylacetylene formation has also been obtained which spans nearly five orders of magnitude in pressure and approaches closely both high and low pressure limiting behaviour (at 495 K).

The significance of these results for the direct allene to methylacetylene isomerisation is discussed; for this purpose a table of thermodynamic properties of cyclopropene is also included.

The kinetics of thermal isomerisation or decomposition of small ring organic compounds has contributed significantly to theoretical understanding of unimolecular reactions. Cyclopropane, cyclobutane and cyclobutene have all been studied both at their high pressure limits and in their " fall-off " regions. The available information is reviewed by Robinson and Holbrook.[1] However, the more strained and less easily handled cyclopropene has been only once investigated. Srinivasan,[2] who carried out this study, found that unless cyclopropene was diluted in a large excess of inert gas, non-homogeneous kinetics result. In $CO_2$ at 60 Torr he obtained a homogeneous first order reaction with

$$\log (k/\mathrm{s}^{-1}) = 12.13-147\ \mathrm{kJ\ mol}^{-1}/RT\ln 10.$$

We have recently proposed [3] that cyclopropene might be implicated as an intermediate in the isomerisation of allene to methylacetylene. To test this idea one requires reliable Arrhenius parameters for cyclopropene pyrolysis. Srinvasan's reported *A* factor appears to be a little low for a ring opening reaction.[1] It is also necessary to see whether allene is present: Srinivasan detected only methylacetylene.

We, therefore, have reinvestigated the kinetics of cyclopropene pyrolysis. We have also studied the unimolecular " fall-off " behaviour since there has been no previous investigation.

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† The authors regret that no reprints are available.

‡ 1 Torr = 133.3 N m$^{-2}$

# EXPERIMENTAL

## APPARATUS

This consisted of a conventional grease free static system with a ≈ 250 $cm^3$ spherical Pyrex reaction vessel placed in a stirred salt thermostat [4] controlled by an AEI (GEC) RT5 controller, temperatures being measured with calibrated Pt/Pt 13% Rh thermocouples. Analyses were made by gas chromatography on a Perkin Elmer F11 chromatograph with peak area integration by a ball and disc instrument. At high pressures ($\geqslant$ 5 Torr), pressures were measured by means of an Hg manometer but at lower pressures a pre-calibrated MKS Baraton (Type 170) was used. A packed vessel of 28-fold greater surface-to-volume ratio was used in some experiments.

## MATERIALS

Cyclopropene was prepared by the procedure of Closs and Krantz [5] by the reaction of sodium amide on allyl chloride. After removal of $NH_3$ by passage through $H_2O$, it was distilled several times through Drikold (−78°C) traps and stored at pressures of $\leqslant$ 10 Torr at room temperature. Because it tended to polymerise slowly over periods of several weeks, the gaseous sample was always subjected to trap distillation at −78°C prior to making up the mixtures for kinetic runs. Prepared in this way, the purest samples of cyclopropene contained ≈ 0.2% allene and ≈ 1% of methylacetylene. Propane, sulphur hexafluoride (Matheson instrument grade), both $\geqslant$ 99% pure, were degassed before use, but not otherwise purified. Nitrogen was B.D.H. (white spot).

## PROCEDURE

The reaction was studied using propane as an internal standard. Half-litre reservoirs containing between 0.5 and 3% of cyclopropene and an approximately equal quantity of propane, diluted in either $SF_6$ or $N_2$ (to a pressure of usually several hundred Torr) were made up and premixed to serve as the reactant mixture. Runs were carried out by admitting a known pressure of this mixture to the reaction vessel for a known time (between 10 min and 3 h). The reaction was quenched by sharing the reaction vessel contents with a pre-evacuated sample bulb, which was then used for product analysis. Every run was accompanied by a blank analysis of the unused reaction mixture sampled from the handing line after sharing into the reaction vessel to ensure that we knew the ratio, cyclopropene to propane, prior to any run. (In a given reaction mixture this ratio would decline by about 10% over a period of two to three weeks.)

## ANALYSIS

Chromatographic analyses were carried out routinely on a 5 m × 3 mm diameter $\beta,\beta'$-oxydipropionitrile-bonded Porasil C column (Waters Associates) operated at room temperature, which readily resolved propane, cyclopropene, allene and methylacetylene (the last two being the reaction products). Although not formed in this reaction, propylene was also separated (eluting between cyclopropene and allene) from other peaks. Products were identified by retention time comparison with authentic samples both on this column and also on a 6 m × 3 mm diameter, 20% hexanedione column operated at 0°C. All $C_3H_4$ isomers were assumed to have the same flame ionisation detector response factors.

In all kinetic runs the analyses of the blank samples were used to correct the product analyses for small amounts of allene and methylacetylene present initially. All product analyses were carried out in duplicate and the results averaged.

# RESULTS

## GENERAL TRENDS IN PRODUCT FORMATION WITH CONDITIONS

Preliminary experiments were carried out at 494.6±0.2 K. The product time evolution was obtained at a fixed starting pressure for mixtures of cyclopropene in both nitrogen and $SF_6$. These results are shown in table 1. In agreement with Srinivasan, methylacetylene is seen to be the principal product. However, small quantities of allene are additionally formed. From the ratio $\Sigma[C_3H_4]/[C_3H_8]$ it can be seen that there is a small mass deficit which increases with time. The cyclopropene and methylacetylene percentages fit reasonably well to integrated first order plots, although with a higher rate constant for the $SF_6$ than the $N_2$ mixture, in qualitative accordance with relative collisional expectations for a unimolecular reaction not at its high pressure limit.

TABLE 1.—PRODUCT VARIATION WITH TIME

| | product %[a] | | | | |
|---|---|---|---|---|---|
| time/min | $c\text{-}C_3H_4$ | All | MA | $\frac{\Sigma[C_3H_4]}{[C_3H_8]}$ | $\frac{[All]}{[MA]}$ |
| | 1.52 % $c\text{-}C_3H_4$ in $N_2$ (initial pressure 74 Torr) | | | | |
| 0[b] | 100 | 0 | 0 | 28.1 | — |
| 10 | 83.7 | 1.6 | 14.8 | 25.8 | 0.106 |
| 20 | 68.3 | 2.2 | 29.5 | 24.3 | 0.075 |
| 30 | 56.8 | 2.5 | 40.8 | 23.4 | 0.062 |
| 45 | 42.3 | 2.4 | 55.2 | 24.2 | 0.004 |
| | 2.83 % $c\text{-}C_3H_4$ in $SF_6$ (initial pressure 63 Torr) | | | | |
| 0[b] | 100 | 0 | 0 | 1.89 | — |
| 20 | 57.6 | 0.27 | 42.2 | 1.63 | 0.006 |
| 30 | 43.6 | 0.37 | 56.1 | 1.54 | 0.0066 |
| 45 | 27.6 | 0.48 | 71.9 | 1.53 | 0.0067 |

[a] All = allene, MA = methylacetylene. [b] Blank mixture corrected for impurity allene and methylacetylene.

TABLE 2.—PRODUCT VARIATION WITH PRESSURE[a] ($N_2$ MIXTURE)

| | | product % | | | | |
|---|---|---|---|---|---|---|
| pressure /Torr | $[c\text{-}C_3H_4]_0$ /Torr | $c\text{-}C_3H_4$ | All | MA | $\frac{\Sigma[C_3H_4]^b}{[C_3H_8]}$ | $\frac{[All]}{[MA]}$ |
| 24 | 0.36 | 77.8 | 2.3 | 19.8 | 27.0 | 0.118 |
| 73 | 1.11 | 68.3 | 2.2 | 29.5 | 24.3 | 0.075 |
| 98 | 1.49 | 66.6 | 2.2 | 31.3 | 23.9 | 0.069 |

[a] See text for reaction conditions. [b] Blank ratio = 27.5 ± 0.5.

Table 2 shows the effect of pressure variation (in the $N_2$ mixture) at a constant reaction time. The increase in conversion of cyclopropene to methylacetylene with pressure supports a pressure-dependent unimolecular reaction. Additionally, the mass deficit increases with increasing pressure. Similar effects were observed in $SF_6$ mixtures (see table 4). The non-constancy of the ratio [All]/[MA] in both tables 1 and 2 shows its formation to be complex.

These observations were explored and tested in detail as described below.

## CORRECTION OF THE FIRST ORDER REACTION FOR MASS LOSS

The observation of a mass loss which increases with time and partial pressure of cyclopropene requires a process of order higher than one. As a working hypothesis a second order process was assumed. Thus the disappearance of cyclopropene can be described by eqn (1),

$$-(\mathrm{d}p/\mathrm{d}t) = k_1p+k_2p^2 \qquad (1)$$

where $p$ is the partial pressure of cyclopropene and $k_1$ and $k_2$ are the rate constants for first order isomerisation and second order mass loss respectively. Although this equation cannot be solved in closed form for $k_1$ and $k_2$, these rate constants can be obtained by iteration. Details are given in the Appendix. Rate eqn (1) was tested qualitatively against the time and pressure dependences of the reaction. A test of the time dependence is shown in table 3. At a given pressure $k_1$ remains reasonably constant with time, thus supporting the first order nature of the methylacetylene formation (up to 70 % conversion).

TABLE 3.—SINGLE RUN RATE CONSTANTS AS A FUNCTION OF TIME [a]

| pressure /Torr | time /min | $r$ [b] | $s$ [c] | $\alpha$ [d] | $10^4k_1/\mathrm{s}^{-1}$ | $10^4k_2$ /Torr$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 17.7 | 10 | 0.805 | 0.957 | 0.26 | 3.55 | 4.12 |
| 17.1 | 31 | 0.513 | 0.984 | 0.044 | 3.56 | 0.73 |
| 17.2 | 45 | 0.374 | 0.976 | 0.058 | 3.60 | 0.96 |
| 62 | 10 | 0.768 | 0.897 | 0.585 | 4.20 | 3.31 |
| 62 | 30 | 0.436 | 0.864 | 0.41 | 4.31 | 2.25 |
| 62 | 45 | 0.305 | 0.836 | 0.46 | 4.07 | 2.53 |

[a] 1.26 % c-$C_3H_4$ in $SF_6$ mixture. [b] $r$ = [c-$C_3H_4$]/Σ[$C_3H_4$]. [c] $s$ = fractional mass recovery (see Appendix). [d] $\alpha = k_2p_0/k_1$ (see appendix).

$k_2$, on the other hand, varies erratically. However, mass loss is a minor process, and the precision of $k_2$ depends significantly on $(1-s)$ (see table 3 footnote and Appendix). The test of pressure dependence of eqn (1) is shown in table 4. Here $k_1$ varies with the total pressure in a way characteristic of a unimolecular process

TABLE 4.—SINGLE RUN RATE CONSTANTS AS A FUNCTION OF PRESSURE [a, b]

| pressure /Torr | $r$ | $s$ | $\alpha$ | $10^4k_1/\mathrm{s}^{-1}$ | $10^4k_2$ /Torr$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 2.37 | 0.716 | 0.944 | 0.25 | 1.80 | 6.72 |
| 4.10 | 0.654 | 0.958 | 0.155 | 2.32 | 3.1 |
| 7.8 | 0.597 | 0.942 | 0.195 | 2.79 | 2.47 |
| 16.5 | 0.524 | 0.980 | 0.057 | 3.56 | 0.43 |
| 25 | 0.499 | 0.926 | 0.22 | 3.72 | 1.16 |
| 42 | 0.459 | 0.879 | 0.37 | 4.08 | 1.25 |
| 62 | 0.436 | 0.838 | 0.51 | 4.26 | 1.22 |
| 112 | 0.381 | 0.795 | 0.66 | 4.83 | 1.01 |
| 199 | 0.356 | 0.657 | 1.40 | 4.78 | 1.19 |
| 413 | 0.380 | 0.796 | 0.65 | 4.87 | ≈ 1.0 |

[a] 2.83 % c-$C_3H_4$ in $SF_6$ mixtures (except for highest pressure run which was diluted 3.8 fold). Reaction time = 30 min. [b] For definitions of $r$, $s$ and $\alpha$ see table 3 and Appendix.

but $k_2$, although erratic at low pressures, tends to be constant at high pressures, where the mass loss process is greatest and the uncertainty in $k_2$ is least. Also, $k_2$ is independent of inert diluent at high pressures. Thus the second order behaviour of the mass loss process is supported under the conditions of maximum mass loss. The erratic behaviour of $k_2$ at small mass deficits does not weaken support for eqn

(1). Since the precision of $k_1$ is of interest, we illustrate the effect of uncertainty in the mass loss. If the run at a total pressure of 16.5 Torr in table 4 had a fractional mass recovery of 0.95 instead of 0.98 (on the limit of experimental precision) then $k_1$ would become $3.50 \times 10^{-4}$ s$^{-1}$ (instead of $3.56 \times 10^{-4}$ s$^{-1}$) and $k_2 = 1.18 \times 10^{-4}$ Torr$^{-1}$ s$^{-1}$ (instead of $0.43 \times 10^{-4}$ Torr$^{-1}$ s$^{-1}$). Thus $k_1$ is negligibly affected but $k_2$ significantly so. In fact even if the mass loss process is not precisely second order it will not seriously affect the values of $k_1$ which are of prime interest in this work.

TABLE 5.—FURTHER CHECKS ON RATE DATA[a]

| pressure /Torr | $10^4k_1$/s$^{-1}$ | $10^4k_2$ /Torr$^{-1}$ s$^{-1}$ | comment |
|---|---|---|---|
| 62 | 4.31 | 2.25 | unpacked Vessel 1 |
| 57 | 4.25 | 1.18 | unpacked Vessel 2 |
| 63 | 4.15 | 2.18 | unpacked Vessel; 0.2 Torr added $O_2$ |
| 64 | 4.22 | 4.02 | packed vessel |
| 25 | 3.80 | — | unpacked vessel, excess *cis*-but-2-ene inhibitor added[b] |
| 72 | 4.53 | 0.51 | |
| 202 | 4.87 | 0.96 | |

[a] 1.26% c-$C_3H_4$ in $SF_6$ mixture. Reaction time = 30 min. [b] Inhibitor in 5.2, 1.6 and 20 fold excess over c-$C_3H_4$ in these runs respectively.

Further checks are summarized in table 5, which confirms that the first order reaction is independent of the particular apparatus used, of the addition of small amounts of oxygen and of the vessel surface-to-volume ratio. The value of $k_2$ seems to be increased more than trivially by an increased surface-to-volume ratio. The table also includes data for three runs in which *cis*-but-2-ene was introduced in excess (over cyclopropene) to test for possible radical scavenging. Comparison of

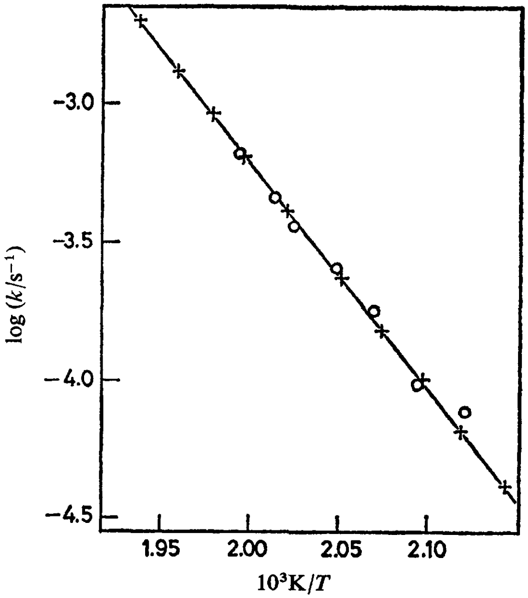


FIG. 1.—Arrhenius plot for methylacetylene formation: +, this work; ○, data of ref. (2).

$k_1$ at the given total pressures with the appropriate data for $k_1$ in table 4 shows that $k_1$ is not affected by the addition of inhibitor, within experimental error.

These results support the view that cyclopropene to methylacetylene isomerisation is a homogeneous unimolecular reaction. They also suggest that mass loss is a second order process.

## HIGH PRESSURE UNIMOLECULAR ARRHENIUS EQUATION

A study was also conducted of the temperature dependence of $k_1$ over the range 466-516 K, using mixtures containing $\sim 1\%$ of cyclopropene in $SF_6$ at a pressure of $70 \pm 2$ Torr. This pressure was chosen to give rate constants near the high pressure limiting value for $k_1$ (in fact 15-20 % below it from table 4). Four runs were carried out at each of ten temperatures, with reaction extents varying between 25 and 75 %. $k_1$ values were calculated for each run, as described previously. Mass losses were generally small ($< 15\%$) but reached 30 % at the lowest temperature and longest time. The rate constants were fitted to an Arrhenius equation, as plotted in fig. 1. The least mean squares line corresponds to

$$\log(k_1/\mathrm{s}^{-1}) = (13.095 \pm 0.038) - (156.1 \pm 0.4 \text{ kJ mol}^{-1})/RT \ln 10$$

where the error limits are one standard deviation. Srinivasan's data [2] are also shown. Although the best Arrhenius line through his data is different from that through ours, the individual rate constants are in close agreement.

## UNIMOLECULAR ALLENE FORMATION

The preliminary experiments demonstrated both a time and pressure dependence of the ratio [All]/[MA]. A unimolecular pathway to allene formation should lead to a ratio independent of these variables (providing the reaction is not too far into its " fall-off " region). Thus we suspect at least two separate pathways to allene formation. If a radical pathway is involved, the addition of inhibitors should lead to reduction in the ratio [All]/[MA]. When *cis*-but-2-ene was introduced into the vessel in 2.3-fold excess over cyclopropene (in $SF_6$, $T = 494.7$ K, $P$(total) = 72 Torr, conversion = 56 %) the ratio [All]/[MA] fell from 0.0049 in the absence of inhibitor to 0.0027 in its presence, a change well outside the experimental uncertainty of this ratio ($\approx \pm 0.0005$). A 20-fold excess of added *cis*-but-2-ene under the same conditions also reduced the ratio to 0.0027. Table 6 shows the results of a set of experi-

TABLE 6.—EFFECT OF ADDED TOLUENE ON ALLENE FORMATION

| pressure /Torr | toluene /Torr | time/min | product % $c\text{-}C_3H_4$ | $\frac{[\mathrm{All}]}{[\mathrm{MA}]}$ |
|---|---|---|---|---|
| 42 | 2 | 10 | 79.2 | 0.0018 |
| 70 | 2 | 10 | 77.0 | 0.0023 |
| 43 | 2 | 30 | 49.3 | 0.0027 |
| 70 | 2 | 30 | 46.1 | 0.0029 |
| 113 | 2 | 30 | 41.9 | 0.0031 |
| 162 | 2 | 30 | 39.4 | 0.0044[a] |
| 42 | 2 | 47 | 32.5 | 0.0021 |
| 52 | 2 | 47 | 31.3 | 0.0027 |
| 70 | 2 | 47 | 28.8 | 0.0026 |
| 113 | 2 | 47 | 26.6 | 0.0030 |
| 164 | 2 | 47 | 24.8 | 0.0029 |

[a] This point not included in the average.

ments in which toluene was used as the inhibitor; it can be seen that, independent of total pressure and time, the ratio is reduced to approximately the same figure (an average of 0.0026±0.0005, excepting one point). In the packed reaction vessel a ratio of 0.0023±0.0005 was obtained after an initial conditioning period of four runs when higher values resulted.

Thus these experiments support the view that a radical component of the reaction is operative in allene formation. They further point to an uninhibitable limiting allene formation, just within the detection limits of our experiments. The independence of the limiting ratio of [All]/[MA] of reaction conditions argues in favour of a parallel unimolecular pathway to allene formation.

In view of the small quantity of allene and its attendent uncertainty, a study of its temperature variation was not warranted.

## PRESSURE DEPENDENCE OF METHYLACETYLENE FORMATION

It has been established that methylacetylene formation is a unimolecular reaction; the results demonstrate that the first-order rate constant is pressure dependent. This reaction thus provides a test of the theory of unimolecular reactions by means of comparison with an extended study of the " fall-off " behaviour.

Experiments were carried out using the same internal standard high dilution mixtures. Rate constants were obtained from single runs to approximately 50% conversion using the same technique to correct for mass loss and, in addition, with correction for allene formation, which amounted to ≈ 10% in some cases at low pressures. Pressures, ($P$),below 5 Torr were measured on the Baratron: mixture compositions were adjusted to give sufficient quantity of material for reliable analysis (*viz*, at 5 Torr > $P$ > 0.1 Torr, 10% cyclopropene containing mixtures: at 0.1 Torr > $P$ > 0.01 Torr, 25% cyclopropene containing mixtures). A larger reaction vessel (0.50 dm$^3$) was used for runs in the lowest pressure range ($P$ < 0.1 Torr). The results for these measurements, both with $SF_6$ and $N_2$ diluent, are shown in fig. 2. These demonstrate the typical rate constant pressure dependence expected of a unimolecular reaction and, in the case of the $SF_6$ diluted mixtures, span nearly five orders of magnitude in pressure and two orders of magnitude in the rate constant. Because of the risk of mechanistic complications at low pressure two runs were

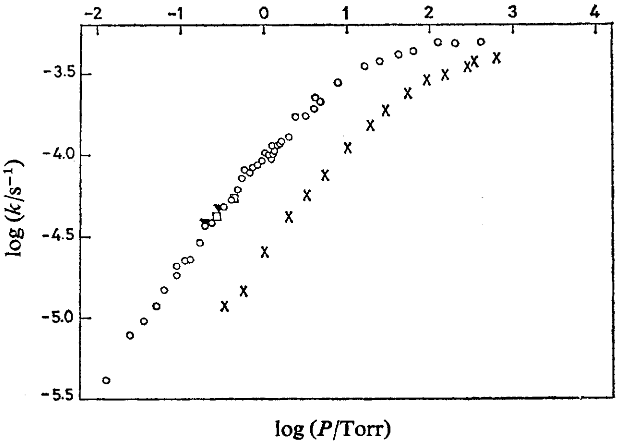


FIG. 2.—Pressure dependence of the rate constant for methylacetylene formation: ○, $SF_6$ mixture; □, packed vessel; ▼, with added toluene; ×, $N_2$ mixture.

carried out with added toluene (to test for possible radical catalysed formation of methylacetylene) and two further runs were carried out in the packed vessel. The rate constants for these runs are consistent with the rest and, therefore, at pressures at least as low as 0.2 Torr, homogeneous unimolecular behaviour is maintained. There remains the possibility of other effects at even lower pressures; however, experimental difficulties precluded the carrying out of such tests at the very lowest pressures.

## DISCUSSION

Detailed application of Unimolecular Reaction Theory to cyclopropene isomerisation will be given in Part 2.[6] The discussion here is limited to consideration of the mechanism and the kinetics particularly from a thermochemical viewpoint.

### (i) UNIMOLECULAR REACTION

Our finding that, under conditions of high dilution, cyclopropene pyrolysis consists in large part of a unimolecular isomerisation to methylacetylene confirms in large part the earlier experimental results of Srinivasan.[2] Since Srinivasan did not detect, or take account of, possible mass loss processes, the agreement between the rate constants obtained here and by Srinivasan is fortuitous, resulting from partial compensation between (*a*) non-allowance for mass loss which, if corrected for, would lower Srinivasan's figures and (*b*) the use by us of $SF_6$ as a diluent which, as a more efficient collision partner than the $CO_2$ used by Srinivasan, tends to make our rate constants higher (nearer to the unimolecular high pressure limit).

The Arrhenius parameters obtained are close to the high pressure limiting values, but we have not extrapolated to high pressure because of the unreliability of this procedure. Instead we made a slight adjustment based on theory,[6] giving

$$\log(k_\infty/\mathrm{s}^{-1}) = 13.25 - 156.8\ \mathrm{kJ\ mol}^{-1}/RT\ln 10.$$

At first sight, although our value for the $A$ factor ($10^{13.1}$ s$^{-1}$) is greater than Srinivasan's ($10^{12.1}$ s$^{-1}$), $A_\infty$ is still *apparently* a little low for a ring-opening reaction when compared, for instance, with $A_\infty$ for cyclopropane isomerisation[7] ($10^{15.5}$ s$^{-1}$). A detailed discussion of this question clearly depends on the structure of the transition state (discussed below) but it may be noted there that cyclopropene isomerisation is considerably less exentropic *overall* ($\Delta S°$, 500 K, = +7.6 J K$^{-1}$ mol$^{-1}$) than cyclopropane isomerisation ($\Delta S°$, 500 K, = +31.5 J K$^{-1}$ mol$^{-1}$).

There are good reasons to support the postulate of a biradical mechanism for cyclopropene isomerisation along the lines of that for cyclopropane.[1, 8, 9, *] Both stereochemical and energetic arguments can be put forward. In the first instance, an optically active cyclopropene (1,3-diethyl-) undergoes racemisation about 9 times faster than isomerisation at 450 K.[12] This result is the analogue in the cyclopropane case, of the faster *cis–trans* isomerisation of 1,2-dideutero-cyclopropane,[13] compared to its structural isomerisation.[7, 14] The second argument concerns the activation energy and is based on the traditional thermochemical analysis,[9, 15] details of which are given in the Appendix. The point is that the energy required to form the biradical (128 kJ mol$^{-1}$) is less than the observed value, 156.8 kJ mol$^{-1}$; therefore a biradical is energetically feasible. Despite theoretical objections [16-19] to some of the implications of the thermochemical approach[15] it remains a powerful indicator of likely mechanism. A theoretical calculation of the generalised valence bond type[20] places a biradical close in energy (163 kJ mol$^{-1}$) to the barrier height we observe.

[*] For a recent discussion of the properties of trimethylene see also ref. (10) and for very recent evidence against a freely rotating biradical see ref. (11).

The difference in *A* factors between cyclopropane and cyclopropene can be traced to the difference in entropy between the respective biradical intermediates trimethylene-1,3-diyl ($\dot{C}H_2$—$CH_2$—$\dot{C}H_2$) and 2-methylene-1-vinyl ($\dot{C}H_2$—CH=$\dot{C}$H). The former is very loose with essentially two free rotations while the latter is rather stiff, the single methylene group losing its rotational freedom due to a degree of allyl delocalisation with the double bond.* The transition states for the two reactions differ from the biradicals in having structures showing some degree of H transfer and C—C bond stiffening but since they are so close to their respective biradicals in energy, it is likely that the same entropy arguments apply. There is also a reaction path degeneracy difference of a factor of 6 favouring cyclopropane (12 as against 2 for cyclopropene). These are the major differences accounting for the $\approx 10^{2.3}$ factor ratio in the *A*-factors and, although there are undoubtedly also small differences in vibrational frequency changes in the two cases, no further insight is to be gained by hypothesising their magnitudes (a largely unrealistic exercise). For the purposes of an RRKM calculation in Part 2 [6] a transition state model is easily specified which conforms to the observed *A* factor for cyclopropene isomerisation.

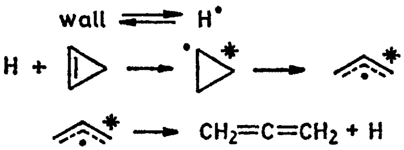
### (ii) MASS LOSS PATHWAY

There is no evidence on the product of this pathway; it must be presumed to be polymer. However, the kinetic indications of a second order reaction are consistent with the initial process of dimerisation discovered by Dowd and Gold [21] *viz.*,

and, as proposed by them, proceeding *via* an " ene " mechanism.

### (iii) ALLENE FORMATION

Most of the allene in the uninhibited reaction appears to be formed by a reaction whose importance decreases with extent of reaction, and with increase in pressure, and furthermore is less important in $SF_6$ than in $N_2$. Although this process has not been investigated in detail, in view of its ready inhibition by *cis*-but-2-ene and toluene, a radical reaction appears to be most likely. Surface sensitivity and the inert diluent dependence support initiation, and maybe also termination, at the wall: we, therefore, suggest the following H atom addition chain process as being most consistent with these facts. In this proposal the reaction is:



propagated *via* vibrationally excited cyclopropyl and allyl radicals respectively. Energy release is sufficient during these reactions to overcome the known energy barriers.

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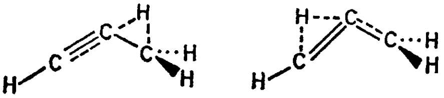
* This is based on the thermochemical energy requirement, although it is not supported by the theoretical calculations of ref. (20).

The minor allene-forming pathway in the presence of inhibitors is first order and homogeneous and is, therefore, likely to be unimolecular. Although Arrhenius parameters were not measured, it is a useful exercise to estimate them since they bear on arguments concerning the direct isomerisation of allene to methylacetylene [see section (iv)]. From cyclopropene the $A$ factors for methylacetylene and allene are likely to be similar in magnitude since the products both arise from 1,2 H shifts in the biradical $\dot{C}H_2—CH{=}\dot{C}H$, (but merely in opposite directions). If the $A$ factors are assumed to be identical, then the measured limiting [All]/[MA] value yields the following Arrhenius equation for allene formation

$$\log(k/\mathrm{s}^{-1}) = 13.25\text{-}181.3\ \mathrm{kJ\ mol^{-1}}/RT\ln 10.$$

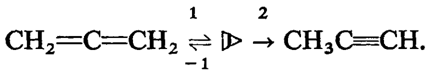
Thus the difference with methylacetylene formation is an activation energy larger by 24.5 kJ mol$^{-1}$. This figure then indicates the relative propensity of the biradical to shift an H-atom in different directions. A possible reason for this large figure can be seen in the resulting transition state structures,



Whereas in the methylacetylene forming reaction, the migrating atom spans a formally single C—C bond, in the allene forming process, a double bond is spanned, resulting in an obviously more strained situation. There is, to our knowledge, no independent evidence concerning such an idea.

### (iv) DIRECT ALLENE TO METHYLACETYLENE ISOMERISATION

We have recently proposed [3] that, in the higher temperature direct allene-to-methylacetylene isomerisation, cyclopropene might be implicated as an intermediate *viz.*,



$$CH_2{=}C{=}CH_2 \underset{-1}{\overset{1}{\rightleftharpoons}} \triangleright \xrightarrow{2} CH_3C{\equiv}CH.$$

The new data obtained in this work are relevant. Since $k_2 > k_{-1}$, the overall rate constant for allene isomerisation is simply $k_1$. From thermodynamic data, $K_{1,-1}$ $(= k_1/k_{-1})$ may be estimated (see Appendix) as

$$\log K_{1,-1}(1100\ \mathrm{K}) = -0.20\text{-}85.2\ \mathrm{kJ\ mol^{-1}}/RT\ln 10.$$

Thus from the experimental $k_{-1}$

$$\log(k_1/\mathrm{s}^{-1}) = 13.05\text{-}266.5\ \mathrm{kJ\ mol^{-1}}/RT\ln 10.$$

The precise Arrhenius parameters depend on an estimated $A_{-1}$ and a long extrapolation, but may be compared with the result of Lifshitz *et al.*,[22]

$$\log(k/\mathrm{s}^{-1}) = 13.17\text{-}253\ \mathrm{kJ\ mol^{-1}}/RT\ln 10$$

(the data of Bradley and West [23] on this reaction have been shown to be in error).[3] The estimated $k_1$ and observed $k$ are not substantially different; at the mid-point of the experimental temperature range, 1125 K, the observed rate constant is a factor of 6 greater than the estimate. On this evidence, therefore, the intermediacy of cyclopropene is not favoured. However, uncertainties in the estimate of $k_{-1}$ combined with experimental errors could easily account for the small difference between $k$ and $k_1$. An experiment is underway to test for the possibility of the intermediacy of cyclopropene in this reaction.[24]

# APPENDIX

## (I) SOLUTION OF MIXED FIRST AND SECOND ORDER RATE EQUATION

$$-(\mathrm{d}p/\mathrm{d}t) = k_1 p + k_2 p^2 \qquad (1)$$

This equation is first expressed in terms of the conveniently measurable quantities;

$r$ = fraction of cyclopropene of the total $C_3H_4$ after time $t$,

$s$ = fractional $C_3H_4$ recovery;

$$s = \left\{\frac{\Sigma[C_3H_4]}{\text{internal standard}}\right\}_t \times \left\{\frac{\text{internal standard}}{[c\text{-}C_3H_4]}\right\}_{t=0}$$

By use of the defined quantity, $\alpha = k_2 p_0/k_1$, where $p_0$ is the initial pressure of cyclopropene, eqn (1) can then be integrated to yield

$$\alpha s(1-\mathrm{r}) = \ln[(1+\alpha)/(1+\alpha s r)]. \qquad (2)$$

Eqn (2) has no explicit analytical solution but was solved interatively until successive values of $\alpha$ differed by $< 0.1\,\%$.

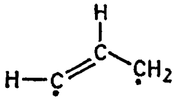
Rate constants are then given by the further equations

$$k_1 = \frac{1}{t}\{-\ln sr - \alpha s(1-r)\}$$

$$k_2 = \alpha k_1/p_0.$$

## (ii) ENERGY(ENTHALPY) REQUIRED TO FORM BIRADICAL

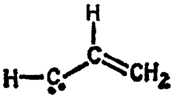
The biradical may be regarded as being formally derived from propylene by removal



of two H atoms in the $C_1$ and $C_3$ positions. In this case

$$\Delta H_f^\circ(\text{biradical}) = \Delta H_f^\circ(C_3H_6) + D(C_1\text{—H}) + D(C_3\text{—H}) - 2\Delta H_f^\circ(\text{H}^\cdot)$$

provided it is assumed that there is no 1,3 electron interaction. The input data (at 298 K) required are as follows: (*a*) $\Delta H_f^\circ(C_3H_6) = 20.4$ kJ mol$^{-1}$.[25] (*b*) $D(C_1-H) = 452(\pm 12)$ kJ mol$^{-1}$. This dissociation energy is not known with certainty. It is equated here to the value for $D(C_2H_3-H)$.[26] (*c*) $D(C_3-H) = 371(\pm 6)$ kJ mol$^{-1}$.[26, 27] Use of this figure implies an allylic stabilisation energy of 42 kJ mol$^{-1}$ in the biradical, that the biradical is in reality a resonance hybrid of the given 1,3 form and of a vinyl carbene form,



We are aware of the theoretical argument against such an assumption.[20] However, it is a premise of the thermochemical approach that no account is taken of wave mechanical spin and symmetry arguments and, therefore, we include the stabilisation effect. (*d*) $\Delta H_f^\circ(\text{H}\cdot) = 218.0$ kJ mol$^{-1}$.[28]

Substitution of these data yields,

$$\Delta H_f^\circ(\text{biradical}) = 407(\pm 13)\ \text{kJ mol}^{-1}$$

which, taken with $\Delta H_f^\circ$(cyclo-$C_3H_4$) = 279 kJ mol$^{-1}$,[29] yields, $\Delta H^\circ$(298 K) = 128(±13) kJ mol$^{-1}$ for the process

$$\text{cyclo-}C_3H_4 \rightarrow \text{biradical.}$$

Correction of this figure to the reaction temperature is not justified. This figure is satisfactorily less than the observed activation energy of 157 kJ mol$^{-1}$ (see text).

### (iii) SOME RELEVANT THERMODYNAMIC PROPERTIES

Thermodynamic data for methylacetylene, allene, propylene and cyclopropane were taken from Stull, Westrum and Sinke [25] [*n.b.* the value for $\Delta H_f^\circ$(cyclo-$C_3H_4$) [29] is incorrectlyq uoted in ref. (25)]. However, no complete tabulation of the properties of cyclopropene is available in the literature [see however ref. (30) and (31) for a partial listing] and so from the available structural and spectral data [30, 32] we have calculated the thermodynamic functions shown in table 7.

TABLE 7.—IDEAL-GAS THERMODYNAMIC FUNCTIONS OF CYCLOPROPENE

| $T$/K | $C_p^\circ$/J K$^{-1}$ mol$^{-1}$ | $S^\circ$/J K$^{-1}$ mol$^{-1}$ | $-\{G^\circ(T)-H^\circ(298.15\text{ K})\}/T$ /J K$^{-1}$ mol$^{-1}$ | $\{H^\circ(T)-H^\circ(298.15\text{ K})\}/T$ /J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| 298.15 | 52.91 | 243.13 | 243.13 | 0 |
| 300 | 53.20 | 243.46 | 243.13 | 0.33 |
| 400 | 67.93 | 260.82 | 245.40 | 15.42 |
| 500 | 80.43 | 277.36 | 250.15 | 27.21 |
| 600 | 90.56 | 292.96 | 256.00 | 36.95 |
| 700 | 98.89 | 307.56 | 262.33 | 45.23 |
| 800 | 105.88 | 321.23 | 268.85 | 52.38 |
| 900 | 111.85 | 334.06 | 275.39 | 58.67 |
| 1000 | 116.99 | 346.12 | 281.87 | 64.25 |

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