Gas-phase Kinetics of Pyrolysis of 1,2-Dimethylcyclopropene

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The pyrolysis of 1,2-dimethylcyclopropene has been studied in the temperature range 260—300 °C. The sole product is isoprene and material recovery was complete to within ±3.5%. The reaction obeyed first-order kinetics and appeared to be homogeneous in a hexamethyldisilazane-conditioned Pyrex reactor, although surface catalysis could not be eliminated in a packed vessel. At 12 Torr (close to the high-pressure limit) rate constants fitted the Arrhenius equation (i). This study provides further evidence for the

$$\log(k/\mathrm{s}^{-1}) = (13.63 \pm 0.19) - (183.7 \pm 2.0\,\mathrm{kJ\,mol^{-1}})/RT\ln 10 \qquad \text{(i)}$$

deactivating effect of methyl substituents on cyclopropene isomerization.

The study of small prototype strained-ring organic compounds has contributed both to a theoretical understanding of unimolecular reactions[1] and to a mechanistic understanding of hydrocarbon isomerizations.[2,3] As part of our continuing work on cyclopropenes,[4—7] we report details of a study of the thermal decomposition of 1,2-dimethylcyclopropene (DMCP). Despite the investigation by Srinivasan[8,9] of the pyrolysis of a number of methylated cyclopropenes, no study of this particular compound has ever been reported. Apart from intrinsic interest we were led to investigate its kinetics for two reasons.

First, the absence of an olefinic hydrogen atom means that the preferred acetylene-forming pathway in other cyclopropenes (Scheme 1) is no longer accessible. Hydrogen atoms are known to have much greater migratory aptitudes than alkyl groups. Thus another pathway, almost certainly of higher energy, is forced to open. Secondly, in order to understand the results of chemical activation experiments involving methylene (CH_2, $^1A_1$ state) addition to but-2-yne,[10] it is necessary to have a reliable knowledge of the energy barrier to isomerization.

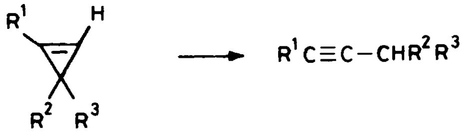
Experimental

Apparatus.—This was as previously described,[7] except for the use of a Perkin-Elmer F33 gas chromatograph.

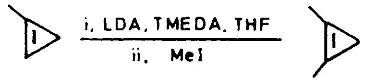
Experimental Procedure.—This was as previously described,[7] except that propane was used as internal standard. One small (*ca.* 0.8%) impurity was observed on the chromatograms of both blanks and runs. This did not interfere with analyses and its constant percentage was taken to indicate no interference with the reaction under study.

Analysis.—The chromatographic analyses were carried out routinely on a 6 m × 3 mm (diam.) 15% w/w β,β′-oxydipropionitrile on 60—80 mesh Chromosorb P column, operated at 25 °C, with a nitrogen carrier gas pressure of 1.1 bar. The identification of the products was confirmed by retention time comparison with authentic samples; typical retention times were: propane 5 min; DMCP, 14 min; 3-methylbuta-1,2-diene (1,1-dimethylallene) 16 min; 2-methylbuta-1,3-diene (isoprene) 17.5 min. It was assumed that all C_5H_8 isomers had the same response factors.

Materials.—Previously described preparations[11—13] of 1,2-dimethylcyclopropene gave poor and irreproducible yields despite a number of efforts by us, and therefore a new synthesis was attempted and developed. The method was based on the methylation of the 1-methylcycloprop-2-enyl anion prepared by the use of lithium base. For this purpose effective deprotonation of 1-methylcyclopropene (MCP) was achieved by use of lithium di-isopropylamide (LDA) (n-butyl-, t-butyl-, or methyl-lithium alone gave negative results). To enhance the rate of lithiation, tetramethylethylenediamine (TMEDA) was added to form a chelate complex.[14] By this method (Scheme 2) yields of *ca.* 75% were achieved. At room temperature DMCP undergoes slow polymerization, but it is stable below 0 °C.



Scheme 1.



Scheme 2.

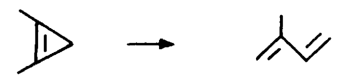
Experimental synthetic details were as follows. n-Butyllithium (30 ml) at −78 °C was slowly added to a stirred mixture of di-isopropylamine (7.8 ml, 0.048 mol) and tetrahydrofuran (THF) (30 ml). After 1 h the solution was warmed to −20 °C and TMEDA (14 ml, 0.051 mol) was added. In a second flask MCP (4.8 g, 0.089 mol) in THF (10 ml) was stirred at −20 °C, and the lithium di-isopropylamide–TMEDA solution was added dropwise. After a further 2 h stirring (during which the solution warmed to 0 °C) the flask contents were quenched with iodomethane (12.62 g, 0.094 mol). The product was worked up by bulb-to-bulb condensation followed by preparative gas chromatography (squalane column, 4.5 m, 15% on Chromosorb W, room temp.) The final product (98.5% pure) contained *ca.* 0.55% isoprene, *ca.* 0.15% dimethylallene, and *ca.* 0.85% of an unknown product.

The DMCP was characterized by gas-phase i.r. spectroscopy g.l.c.–mass spectrometry (details in ref. 15), and n.m.r. [δ_H 1.98 (s, 6 H) and 0.78 (s, 2 H); δ_C 105.90 (olefinic), 11.18 (Me), and 8.62 (ring methylene)].

Table 1. 1,2-Dimethylcyclopropene time decay data

Temp. (°C)								10^4 k/s^{-1}
260.0	Time (min)	60	120	210	300	570		0.424 ± 0.003
	%	86.91	74.07	58.03	46.66	23.61		
270.0	Time (min)	30	60	100	165	220	300	0.949 ± 0.006
	%	85.91	71.75	57.70	39.62	29.18	18.17	
279.7	Time (min)	15	30	50	75	110	150	1.829 ± 0.020
	%	82.55	70.48	57.21	44.42	29.82	18.83	
289.7	Time (min)	8	15	25	40	55	75	3.83 ± 0.07
	%	81.61	69.74	56.59	38.37	29.25	17.38	
300.0	Time (min)	5	10	15	20	25	35	7.75 ± 0.16
	%	79.35	61.30	49.97	41.16	30.04	19.70	

Table 2. Comparison of high-pressure rate constants

Reaction	log (A/s^{-1})	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} ^{a}	E_a/kJ mol^{-1} (kcal mol^{-1})	10^4 k/s^{-1} ^{a}	Ref.
	13.25	−3.9	157 (37.5)	7.41	5
	12.72	−14.0	158 (37.8)	1.62	7
	13.48	+0.5	177 (42.2)	0.106	7
	13.49	+0.7	183 (43.8)	0.0218	7
	13.63	+3.4	184 (43.9)	0.0275	This work

^{a} At 500 K.

Propane and sulphur hexafluoride (Matheson Instrument Grade) both ⩾99% pure were degassed before use. Nitrogen (British Oxygen, white spot) contained no detectable impurity.

Results

General Considerations.—Because of problems encountered previously with cyclopropene itself,[5] neat reactant vapour was not used in these experiments. Instead mixtures containing DMCP (*ca.* 5—6%) and propane (*ca.* 5—6%) highly diluted in SF_6 were made up. This dilution reduced the risk of polymerization and the propane served as a non-reactive internal standard to enable checks to be made of the mass balance after a reaction run. In the majority of over 70 runs, recovery of the C_5H_8 isomers was 100 ± 3.5% of the original DMCP. In this respect DMCP resembled MCP but not cyclopropene itself,[5] which did give rise to mass-losing side-reactions under these conditions. The reaction was extremely surface sensitive and for reliable kinetic studies it was necessary to condition the vessel regularly by exposure to hexamethyldisilazane (HMDS). For convenience, and to avoid a risk of deconditioning during a run, about 5 Torr of HMDS was left in the reaction vessel for 15—30 min before each run. This procedure ensured that reproducible minimum rates were always obtained. The only reaction product found was isoprene, although small amounts ($\leqslant$0.1% of the total C_5H_8) of dimethylallene were also formed in some runs.

Kinetic Measurements.—The time dependence of the reaction was investigated at each of five temperatures at a constant initial (mixture) pressure of 12 ± 1 Torr up to over 80% conversion. For kinetic purposes a correction was made for the isoprene and dimethylallene impurities in DMCP but the small and erratic (<0.1%) yields of dimethylallene were not taken into account. Table 1 shows the % reactant–time data obtained. At each temperature these data were found to give good fits to a first-order plot; the rate constants found by least-mean-squares fitting are also shown in the Table.

Because small molecules may show characteristic pressure dependences of their first-order rate constants[1] an attempt to investigate this was made. Mixtures at pressures between 5.6 and 72.6 Torr were pyrolysed for 15 min at 279.7 °C. Unfortunately these runs were carried out before it was realized how surface-active the reaction was (see later) Thus all these runs gave slightly higher conversions (18.0—23.6%) than subsequently found at this temperature. However, there was no obvious trend in the data, suggesting that over this pressure range there were no large pressure dependences (of the homogeneous part of the reaction). For MCP the onset of pressure dependence (in SF_6) appeared to be in the region 10—20 Torr.[7] A lower pressure for onset of the 'fall-off' phenomenon would be expected for the larger DMCP molecule, and to this extent this conclusion is reasonable. The use of 12 Torr total pressure in the systematic time dependence studies was expected to ensure that rate constants were at or close to the high-pressure limit. Since high-pressure rate parameters were the main aim of this work, a low-pressure study of the 'fall-of' phenomenon, in a properly deactivated vessel, was not deemed worthwhile.

The first-order rate constants shown in Table 1 were fitted to the Arrhenius equation, a plot of which is shown in the Figure.

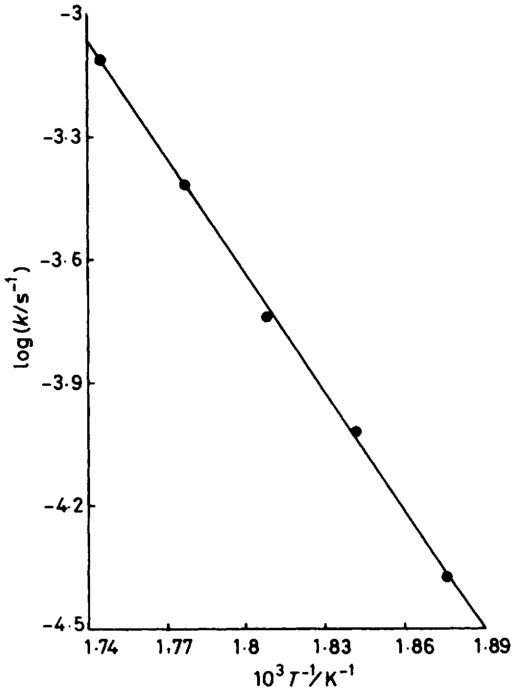


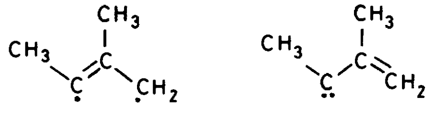
Figure. Arrhenius plot

A least-mean-squares fit to the data gave equation (i), where the

$$\log(k/\mathrm{s}^{-1}) = (13.63 \pm 0.19) - (183.7 \pm 2.0\ \mathrm{kJ\ mol^{-1}})/RT\ln 10 \quad \text{(i)}$$

error limits represent one standard deviation.

Early experiments in the vessel without HMDS treatment showed surprisingly good first-order behaviour with rate constants *ca.* 30% too high. Because of this, experiments were carried out in a packed reaction vessel (surface-to-volume ratio 4.9 $\mathrm{cm^{-1}}$) well conditioned with HMDS. A study of the time-dependence at 270 °C gave a good first-order fit with $k = 2.89 \times 10^{-4}\ \mathrm{s^{-1}}$, a factor of 3 higher than the rate in the unpacked vessel (surface-to-volume ratio 0.71 $\mathrm{cm^{-1}}$). Thus it appears that this reaction is particularly sensitive to surface catalysis. Reactions in the packed vessel were marked by formation of greater amounts of dimethylallene as well as another (unidentified) product amounting to *ca.* 12% of the total C_5H_8 at 80% conversion. A run in the packed vessel with added propene (*ca.* 100 times the DMCP initial partial pressure) decreased the conversion (and rate) somewhat, indicating inhibition, possibly of a radical component to the reaction under these conditions. Thus the evidence on heterogeneity is equivocal. There is clearly an additional, surface-generated, component to the rate in the packed vessel. In the unpacked vessel, however, in spite of repeated and prolonged treatment with HMDS, no further rate reduction was achieved. The goodness of fit to the Arrhenius equation and the reasonableness of the Arrhenius parameters (see Discussion section) offer some support for the view that, in the HMDS-treated, unpacked vessel, this reaction is not substantially perturbed by surface effects.



(1) (2)

both *trans* and *cis*

Scheme 3.

Discussion

Despite the surface effects, the Arrhenius parameters obtained for this reaction are consistent with those expected for a cyclopropene ring-opening reaction. A comparison of the present work with analogous studies of cyclopropene and 1-methylcyclopropene is shown in Table 2. The *A* factor for DMCP is of the same order of magnitude as those for the other cyclopropenes. Cyclopropenes appear to have consistently lower *A* factors than other ring-opening processes[1] (for example, cyclopropanes). As we have commented previously,[5,7] this may be related to the fact that there is relatively little overall entropy increase in cyclopropene isomerizations ($+8 \pm 4\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for DMCP to isoprene at 500 K).

The magnitude of the activation energy is consistent with the involvement of an intermediate which may be considered to be either a diradical (**1**) or vinylcarbene (**2**) (Scheme 3). A thermochemical estimate[5] suggests that diradical formation (assuming no serious perturbation by methyl groups) requires *ca.* 128 kJ $\mathrm{mol^{-1}}$. Recent elaborate theoretical calculations[16] show that both singlet diradical and carbene states are energetically accessible in the prototype C_3H_4 case.* Both these calculations and a much earlier study of an optically active cyclopropene[17] (which is racemized much faster than it rearranges) indicate that H-migration in the intermediate requires more energy than that needed to produce the intermediate. Thus the H-migration step in the present case, rather than intermediate formation, is likely to be rate-determining.

The effect of methyl group substitution is interesting. A comparison of diene-forming pathways (Table 2) shows that DMCP is nearly 4 times slower than MCP (at 500 K). Since DMCP has two methyl groups, the intrinsic reactivity difference is close to a factor of 8. It is also clear that methyl group substitution slows down the acetylene-forming pathway in MCP (Table 2 and ref. 7). This methyl group deactivating effect in cyclopropenes stands in contrast to the activating effect of methyl groups in cyclopropanes. Possible explanations for this include (i) destabilization of the transition state for H-migration, (ii) destabilization of the intermediate (diradical or carbene form), and (iii) stabilization of the ground-state cyclopropene. Because methyl groups normally stabilize radical centres and because in any case the methyl groups are remote from the carbon atoms involved in the H-migration transition state (see later) neither explanation (i) nor (ii) appeals to us. Moreover the deactivating methyl group is positioned differently in the intermediate for the diene-forming pathway than for the acetylene-forming pathway. Thus if explanation (ii) were

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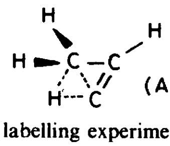
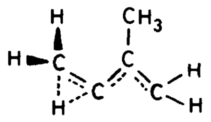
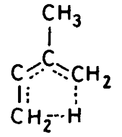
* The calculations also suggest that, in spite of the accessibility of (**1**) and (**2**) the methylacetylene-forming pathway occurs *via* a third intermediate, *viz.* propenylidene, $CH_3CH{=}C$:. produced *via* a transition state structure (A)



(A)

We plan to carry out a labelling experiment to discover whether this pathway occurs.


(3)


(4)

important two different destabilising effects would be required. We therefore favour explanation (iii), that methyl groups stabilize ground-state cyclopropene. Perhaps because the cyclopropene ring is so highly strained, methyl substitution can lower the heat of formation by more than the usual increment for acyclic olefins.

As far as the mechanism is concerned, it is clear that when an acetylene-forming pathway is unavailable the next lowest pathway is that leading to a 1,3-diene. This pathway, a minor process for MCP, becomes the only process for DMCP. Activation energies are *ca.* 20 kJ mol^{-1} higher for this pathway. We have rationalized this increase in terms of the 'H-bridging strain' in the transition state.[7] For DMCP the transition state structure is (**3**) (*transoid* form). In this structure the migrating hydrogen spans a carbon–carbon bond of order one and a half.

The virtual absence of dimethylallene as a product ($\leqslant 10^{-3}$ of isoprene) indicates that a 1,4-shift process is unfavourable. If it occurred, it would require a transition-state structure (**4**). We previously argued[7] that buta-1,2-diene was formed from MCP *via* a 1,2-H-shift rather than a 1,4-H-shift. A 1,2-H-shift to dimethylallene is not possible for DMCP and so the absence of this product confirms our mechanistic preference for this pathway from MCP.[7]

One other non-observed but possible C_5H_8 isomer is methyl(methylene)cyclopropane. This would be formed *via* a 1,3-C–H insertion reaction of the carbene (**2**). Its absence indicates that such insertions are not favoured.

A number of other methylated cyclopropenes have been studied,[9] all with at least one 3-methyl substituent. These conform to the overall reactivity pattern observed here, of decreasing rates with increasing methyl substitution. Diene-formation pathways *via* 1,4-H-shifts from a 3-methyl group appear to be important but the acetylene-formation pathway apparently diminishes in significance rather abruptly with 1,3,3-trimethylcyclopropene. This does not follow the pattern expected from the methyl substitution effects and activation energies established here. In another example, 1,3-diethylcyclopropene,[17] the acetylene-forming pathway-constituted *ca.* 33% of the total products, again a low figure. There are clearly still mysteries requiring explanation in alkylcyclopropene pyrolysis.

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Received 28*th October* 1985; *Paper* 5/1871