Kinetics of the Thermal Gas-phase Decomposition of Methoxycyclopropane

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In the temperature range 635–694 K, 70–80% of the methoxycyclopropane decomposing initially results in the formation of the isomerization products (E)- and (Z)-1-methoxyprop-1-ene and 3-methoxyprop-1-ene. The residual decomposition results from approximately equal contributions from methyl–oxygen bond fission and the subsequent radical abstraction reactions. The isomerization products are formed by homogeneous, non-radical, unimolecular pathways with high-pressure rate constants given by the equations

$$k[(E)\text{-}+(Z)\text{-1-methoxyprop-1-ene}]/\text{s}^{-1} = 10^{13.29 \pm 0.75} \exp\left(-226.5 \pm 9.5 \text{ kJ mol}^{-1}/\boldsymbol{R}T\right)$$

and

$$k(\text{3-methoxyprop-1-ene})/\text{s}^{-1} = 10^{14.0 \pm 1.1} \exp\left(-254 \pm 14 \text{ kJ mol}^{-1}/\boldsymbol{R}T\right).$$

The methoxy group lowers the activation energy for opening the cyclopropane ring adjacent to the point of substitution by *ca.* 45 kJ mol^{-1}.

Although there have been numerous studies of the gas-phase thermal decomposition of substituted cyclopropanes,[1, 2] there have been few examples in these studies of alkoxy-substituted cyclopropanes. However, among them a methoxy substitutent was found to reduce the activation energy for rearrangement of vinylcyclopropane to cyclopentene by *ca.* 46 kJ mol^{-1} in the case of 1-methoxy-2-vinylcyclopropane but to lower the activation energy by only *ca.* 21 kJ mol^{-1} for 1-methoxy-1-vinylcyclo-propane.[3] Also Kirmse and Zeppenfeld[4] measured the rates of geometric isomerization of 1,2-dimethoxy-3-methylcyclopropanes between 260 and 310 °C and found the methoxy substituents promoted the biradical mechanism, rather than the synchronous double rotation mechanism, for cyclopropane isomerization. However, when the same material was pyrolysed at higher temperatures no structural isomerization products were found, even though substantial loss of reactant occurred.[4]

We decided to investigate the thermal decomposition of methoxycyclopropane to see if structural isomerization products analogous to those formed from alkyl cyclopropanes were produced and, if so, to measure the effect of the methoxy substituent on the Arrhenius parameters for the reaction. In addition it was hoped that methoxycyclopropane would decompose *via* competing unimolecular channels and would therefore prove a suitable molecule for investigating the mechanism for intermolecular energy transfer.[5]

EXPERIMENTAL

All thermal kinetic studies were carried out as previously described[6] in a conventional 'static' system using Pyrex reaction vessels aged by pyrolysis of *ca.* 20 Torr† hexamethyldisiloxane at
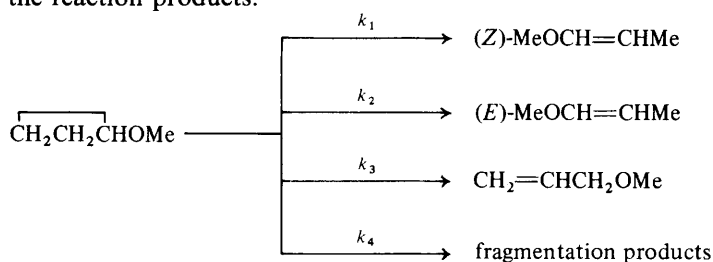
† 1 Torr ≈ 133 N m^{-2}.

525 °C for 24–48 h. Two reaction vessels were employed; one was packed with short lengths of Pyrex tubing to give a surface-to-volume ratio (S/V) of $ca.$ 12 cm^{-1}, the other was of similar external dimensions but was not packed (S/V $ca.$ 1 cm^{-1}, volume $ca.$ 150 cm^3). Young's greaseless stopcocks were used in all parts of the vacuum system in contact with pyrolysed material.

Produce analyses were carried out on a 50 m squalane SCOT column maintained at $ca.$ 0 °C with helium carrier gas. A Pye flame ionization detector coupled to a Pye wide-range amplifier and an LDC 308 computing integrator were used for quantitative determination of the eluted compounds. Sensitivity coefficients for all the identified products were determined by injection of mixtures of known composition onto the chromatographic column. Some analyses were also carried out using a 6 ft, $\frac{1}{4}$ in diameter, Phasepak Q column with katharometer detection. The relative sensitivities for carbon monoxide and methane quoted in ref. (7) were used to estimate the relative amounts of these two compounds using Phasepack Q column. The identity of the reaction products was confirmed using g.l.c./mass spectrometry (Kratos MS 30 mass spectrometer).

Methoxycyclopropane was prepared by the method of Krantz and Drake[8] and purified to 99.85% by fractional distillation on a 0.6 m Podbielniak column followed by preparative chromatography. 1-methoxyprop-1-ene (mixed isomers) was prepared from 1,1-dimethoxy-propane[9] and 3-methoxyprop-1-ene from 3-bromoprop-1-ene.[10] Other chemicals used were commercially available samples.

RESULTS

Over the temperature range 635–694 K methoxycyclopropane decomposed to give (E)- and (Z)-1-methoxyprop-1-ene and 3-methoxyprop-1-ene as isomerization products and other products that had resulted from fragmentation reactions (see scheme 1). The fragmentation products accounted for $ca.$ 30% of the methoxycyclo-propane reacting at the highest temperature but dropped to $ca.$ 20% at the lowest temperature and consisted mainly of carbon monoxide, methanal, methane, ethane, ethene, propene, but-1-ene, pent-1-ene and hexa-1,5-diene. Carbon monoxide and methane were formed in approximately equal amounts. No analyses for hydrogen or quantitative estimates of methanal yields were made. No 2-methoxyprop-1-ene was detected in the reaction products.

$$CH_2CH_2CHOMe \begin{cases} \xrightarrow{k_1} (Z)\text{-MeOCH}{=}\text{CHMe} \\ \xrightarrow{k_2} (E)\text{-MeOCH}{=}\text{CHMe} \\ \xrightarrow{k_3} CH_2{=}CHCH_2OMe \\ \xrightarrow{k_4} \text{fragmentation products} \end{cases}$$

SCHEME 1

First-order rate plots for loss of initial reactant (28 Torr initial reactant pressure) were linear to $ca.$ 60% reaction. However, secondary decomposition of (Z)-1-methoxyprop-1-ene and 3-methoxyprop-1-ene resulted in their product distribution plots (plots of percentage individual product against percentage overall reaction) showing significant negative curvature ($i.e.$ less product was observed at long reaction times than a linear plot would predict) and this made the determination of the individual rate constants for the formation of the isomerization products difficult. In order to minimize this problem the majority of kinetic runs were limited to a maximum of 10% reaction (see fig. 1 and 2 for typical product distribution plots). Direct

determination of the initial rates of formation of the isomerization products from the product distribution plots was still difficult but an alternative plot proved better (see Appendix for further explanation) and also allowed an estimate to be obtained for the rate constant (k_d) for decomposition of 3-methoxyprop-1-ene:
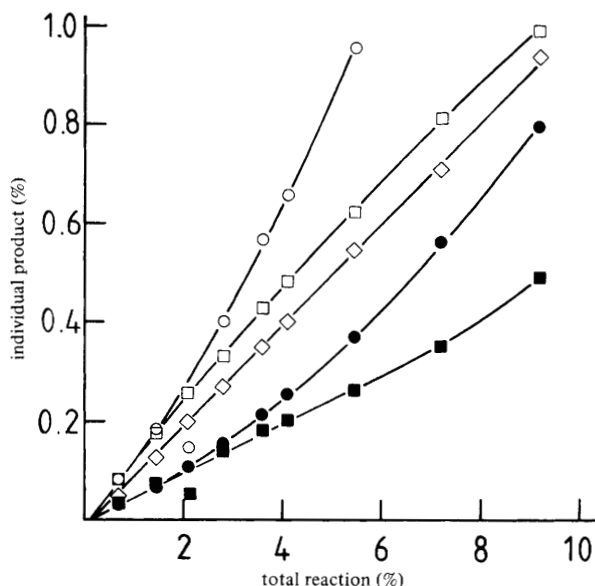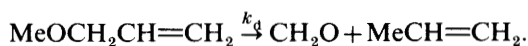
$$\text{MeOCH}_2\text{CH}=\text{CH}_2 \xrightarrow{k_d} \text{CH}_2\text{O} + \text{MeCH}=\text{CH}_2.$$

Fig. 1. Product distribution plot for decomposition of methoxycyclopropane at 28 Torr initial pressure and 645.5 K: $\bigcirc$, methane; $\square$, (Z)-1-methoxyprop-1-ene ($\times 0.2$); $\diamondsuit$, (E)-1-methoxyprop-1-ene; $\bullet$, propene; $\blacksquare$, ethane.

The rate constants so determined are listed in table 1. Rate constants for the formation and loss of 3-methoxyprop-1-ene could only be obtained at five of the seven temperatures studied. In Arrhenius form the rate constants may be expressed as follows:

$$k_{\text{total}}/\text{s}^{-1} = 10^{14.04 \pm 0.99} \exp\left(-234.2 \pm 12.6 \text{ kJ mol}^{-1}/RT\right)$$

$$k_1/\text{s}^{-1} = 10^{13.46 \pm 0.62} \exp\left(-229.5 \pm 7.9 \text{ kJ mol}^{-1}/RT\right)$$

$$(k_1 + k_2)/\text{s}^{-1} = 10^{13.29 \pm 0.75} \exp\left(-226.5 \pm 9.5 \text{ kJ mol}^{-1}/RT\right)$$

$$k_2/\text{s}^{-1} = 10^{12.5 \pm 1.0} \exp\left(-228 \pm 13 \text{ kJ mol}^{-1}/RT\right)\dagger$$

$$k_3/\text{s}^{-1} = 10^{14.0 \pm 1.1} \exp\left(-254 \pm 14 \text{ kJ mol}^{-1}/RT\right)$$

$$k_4/\text{s}^{-1} = 10^{16.2 \pm 0.9} \exp\left(-270 \pm 12 \text{ kJ mol}^{-1}/RT\right)\dagger$$

$$k_d/\text{s}^{-1} = 10^{11.2 \pm 0.8} \exp\left(-180 \pm 11 \text{ kJ mol}^{-1}/RT\right).$$

Error limits quoted are statistical 95% certainty limits. Data for (E)-1-methoxyprop-1-ene is much more scattered than for the (Z)-isomer. However, the ratio of rate

† Data at the six highest temperatures only were used to calculate these parameters.
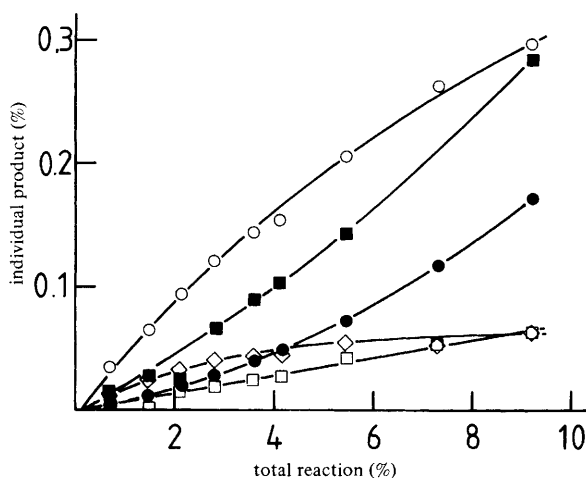
Fig. 2. Product distribution plot for decomposition of methoxycyclopropane at 28 Torr initial pressure and 645.5 K: ○, hexa-1,5-diene; ■, ethene; ●, but-1-ene, ◇, 3-methoxyprop-1-ene; □, pent-1-ene.

Table 1. Rate constants for decomposition of methoxycyclopropane (28 Torr initial pressure) and 3-methoxyprop-1-ene (k_d)

T/K	$k_1/10^{-5}$ s^{-1}	$k_2/10^{-5}$ s^{-1}	$k_3/10^{-6}$ s^{-1}	$k_4/10^{-5}$ s^{-1}	$k_d/10^{-3}$ s^{-1}
694.3	15.6	2.37	7.6	7.9	5.0
681.4	7.16	1.04	—	3.23	—
671.2	4.22	0.635	1.76	1.72	1.85
662.6	2.32	0.371	0.88	0.89	1.13
654.1	1.29	0.202	—	0.44	—
645.5	0.77	0.117	0.259	0.23	0.47
635.8	0.41	0.095	0.139	0.16	0.29

constants for formation of the (Z)- and (E)-isomers would not appear to have a significant temperature dependence and $k_1/k_2 = 6.6 \pm 0.3$.

The pressure dependence of the reactions was studied between 3 and 37 Torr at 662.6 K for 20 min pyrolysis times. The results are shown in fig. 3. The overall reaction rate decreased with decreasing pressure as did the individual rates of formation of the isomerization products and hexa-1,5-diene. The majority of fragmentation products, *i.e.* methane, propene, but-1-ene and pent-1-ene, showed a slight increase as the pressure was decreased.

The effect of nitric oxide on the reaction was investigated at 694 K using 20% nitric oxide added to the initial reactant. The overall reaction rate decreased slightly (*ca.* 8%) although the initial rates of formation of the isomerization products were not affected and the extent of secondary decomposition of these products was also little affected. Thus the isomerization products were almost certainly formed by unimolecular, non-radical, pathways and the secondary decompositions probably did not mainly result from radical induced reactions. All fragmentation products were reduced by the addition of nitric oxide, with the exception of ethane which showed an increased yield, thus indicating the importance of radical pathways in their formation.
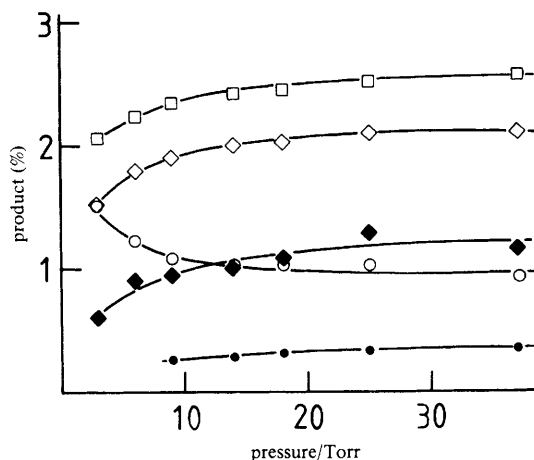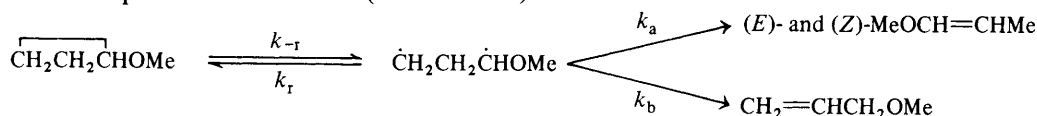
Fig. 3. Pressure dependence of products from the thermal decomposition of methoxycyclopropane (20 min pyrolyses at 662.6 K). □, (Z)-1-methoxyprop-1-ene; ◇, (E)-1-methoxyprop-1-ene (× 2); ◆, 3-methoxyprop-1-ene (× 10); ○, major fragmentation products but excluding hexa-1,5-diene; ●, hexa-1,5-diene.

Kinetic runs at 680 K in the packed reaction vessel with 35 Torr initial reactant gave an overall rate *ca.* 17% faster than in the unpacked reaction vessel; however, the rates of production of the isomerization products were unaffected and the increase in rate was the result of increased fragmentation reactions.

DISCUSSION

The isomerization of methoxycyclopropane to (E)- and (Z)-1-methoxyprop-1-ene and 3-methoxyprop-1-ene has been shown to be the result of a first-order, homogeneous, and probably unimolecular, reactions and to be in competition with fragmentation reactions. The Arrhenius parameters for the reactions were measured in the high-pressure region as unimolecular fall-off is not apparent above *ca.* 10 Torr.

A biradical mechanism is consistent with the formation of the methoxypropenes with the methoxy group lowering the activation energy for opening the ring adjacent to the point of substitution (see scheme 2).

$$\overline{CH_2CH_2\dot{C}HOMe} \underset{k_r}{\overset{k_{-r}}{\rightleftharpoons}} \dot{C}H_2CH_2\dot{C}HOMe \overset{k_a}{\underset{k_b}{<}} \begin{array}{l} (E)\text{- and }(Z)\text{-MeOCH=CHMe} \\ CH_2=CHCH_2OMe \end{array}$$
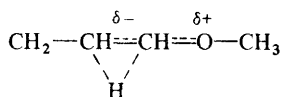
SCHEME 2

The absence of 2-methoxyprop-1-ene, the product that would have resulted from breaking the bond opposite to the point of substitution, suggests that this bond may even be strengthened by the presence of the methoxy group; if the activation energy were the same as that for cyclopropane then the formation of some of this product would have been expected to have been observed. The Arrhenius parameters for the formation of the methoxypropenes have rather large error limits and arguments based on these parameters are therefore necessarily speculative, but the rather low A factor observed for (E)- and (Z)-1-methoxyprop-1-ene (*cf.* 10^{14}–10^{15} s^{-1} for methylcyclopropane[1]) suggests that the effect of the methoxy group is not only to reduce the activation energy but also to lower the 'A' factor; presumably, in stabilizing
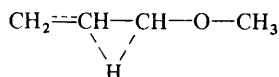
the transition state, rotation of the methoxy group is hindered. In contrast, the 'A' factor and activation energy for 3-methoxyprop-1-ene formation are much closer to those observed for alkyl cyclopropanes and thus in this case, in the transition state for H-atom transfer, the stabilization due to the methoxy group has been lost (see scheme 3).

$$\overset{\delta-}{}\quad\overset{\delta+}{}$$
$$\dot{C}H_2\text{---}CH_2\text{---}\dot{C}H\!\!=\!\!O\text{---}CH_3$$
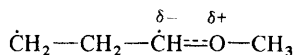
biradical formed from methoxycyclopropane

$$CH_2\text{---}\overset{\delta-}{CH}\!\!=\!\!\overset{\delta+}{CH}\!\!=\!\!O\text{---}CH_3$$
$$\diagdown\;\diagup$$
$$H$$

$$CH_2\!\!=\!\!CH\text{---}CH\text{---}O\text{---}CH_3$$
$$\diagdown\;\diagup$$
$$H$$

transition state for formation of (E)-   transition state for formation of CH_2=$CHCH_2OMe$
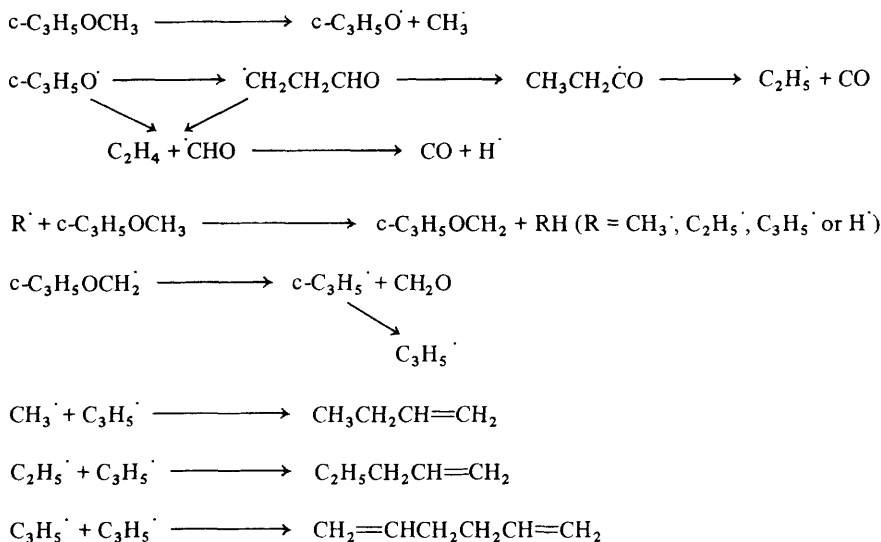and (Z)-MeOCH=CHMe

SCHEME 3

It would seem likely that for the formation of (E)- and (Z)-1-methoxyprop-1-ene the H-atom transfer step of the biradical is fast compared with ring closure, with the methoxy substituent stabilizing the transition state for this reaction as well as for ring opening ($k_1 + k_2 = k_r k_a/(k_{-r} + k_a + k_b) \simeq k_r$ as $k_a \gg k_{-r} + k_b$, scheme 2). Hydrogen-atom transfer to give 3-methoxyprop-1-ene is much slower than that to give the (E)- and (Z)-isomers and in direct competition from the same biradical. Thus the difference in the activation energies and values of log A for the two processes may be equated to the difference in the values of these parameters for the two H-atom transfer steps ($k_3 = k_r k_b/(k_{-r} + k_a + k_b) \simeq k_r k_b/k_a$ as $k_a \gg k_{-r} + k_b$). Thus it would appear that the methoxy group not only lowers the barrier to ring opening by $ca.$ 45 kJ mol^{-1}, relative to unsubstituted cyclopropane, but also lowers the barrier for H-atom transfer in the biradical to give (E)- and (Z)-1-methoxyprop-1-ene by $ca.$ 25 kJ mol^{-1} (the incipient double bond is α to the methoxy group in the transition state for this reaction) relative to the transition state for formation of 3-methoxyprop-1-ene (the incipient double bond is now β to the methoxy group).

Kirmse and Zeppenfeld[4] observed that the activation energy for geometric isomerization of 1,2-dimethoxy-3-methylcyclopropane was $ca.$ 210 kJ mol^{-1}, $i.e.$ 63 kJ mol^{-1} lower than is observed for the geometric isomerization of [1,2-^{2}H$_2$]cyclopropane.[1] If the observed slower rate (by a factor of 100) in the thermal isomerization of 1-methoxy-2,3-dimethylcyclopropane[4] is assigned entirely to a change in the activation energy, it would require the stabilization energy to be reduced by $ca.$ 21 kJ mol^{-1}, $i.e.$ it would give a stabilization energy of 42 kJ mol^{-1} for a single methoxy group, in good agreement with the value we find and with the value of 46 kJ mol^{-1} for 2-methoxy-1-vinylcyclopropane.[3]

In contrast to the alkyl cyclopropanes, methoxycyclopropane undergoes extensive fragmentation reactions in competition with isomerization. From the product analyses it is apparent that methyl, ethyl and allyl radicals are the predominant radicals in the system. From the distribution of products it would seem that approximately half the methoxycyclopropane decomposes as the result of an initial methyl-radical loss and half as the result of subsequent radical attack on the initial reactant. We suggest that the ethyl radical is produced in the subsequent decomposition of the initially formed cyclopropoxy radical. The lack of any methanol in the reaction products indicates that
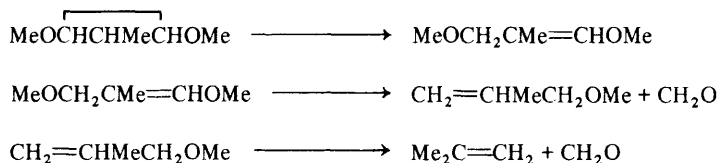
split of the cyclopropyl–oxygen bond does not occur to any appreciable extent. All the major fragmentation products are accounted for by the reaction sequence in scheme 4.

$$c\text{-}C_3H_5OCH_3 \longrightarrow c\text{-}C_3H_5O^{\cdot} + CH_3^{\cdot}$$

$$c\text{-}C_3H_5O^{\cdot} \longrightarrow {}^{\cdot}CH_2CH_2CHO \longrightarrow CH_3CH_2\dot{C}O \longrightarrow C_2H_5^{\cdot} + CO$$

$$C_2H_4 + {}^{\cdot}CHO \longrightarrow CO + H^{\cdot}$$

$$R^{\cdot} + c\text{-}C_3H_5OCH_3 \longrightarrow c\text{-}C_3H_5OCH_2^{\cdot} + RH \ (R = CH_3^{\cdot}, C_2H_5^{\cdot}, C_3H_5^{\cdot} \ \text{or} \ H^{\cdot})$$

$$c\text{-}C_3H_5OCH_2^{\cdot} \longrightarrow c\text{-}C_3H_5^{\cdot} + CH_2O$$

$$C_3H_5^{\cdot}$$

$$CH_3^{\cdot} + C_3H_5^{\cdot} \longrightarrow CH_3CH_2CH{=}CH_2$$

$$C_2H_5^{\cdot} + C_3H_5^{\cdot} \longrightarrow C_2H_5CH_2CH{=}CH_2$$

$$C_3H_5^{\cdot} + C_3H_5^{\cdot} \longrightarrow CH_2{=}CHCH_2CH_2CH{=}CH_2$$

SCHEME 4

The decomposition of alkyl allyl ethers occurs as the result of a retro-ene reaction, *via* a concerted, 6-membered ring, transition state with no evidence for free-radical pathways or charge development in the transition state.[11, 12] The Arrhenius parameters previously determined for the decomposition of 3-methoxyprop-1-ene $[E_a = 174 \text{ kJ mol}^{-1}, \log (A/\text{s}^{-1}) = 11.1]$[12] are in good agreement with those measured in the present study $[E_a = 180 \pm 11 \text{ kJ mol}^{-1}, \log (A/\text{s}^{-1}) = 11.2 \pm 0.8]$ suggesting that little if any of this product can have been lost in our system as a consequence of the radicals present.

As a result of our study the reasons why Kirmse and Zeppenfeld failed to observe vinyl ethers in the thermal decomposition of 1,2-dimethoxy-3-methylcyclopropane at temperatures $> 300\ ^{\circ}C$[4] becomes more apparent. On the one hand, methyl–oxygen bond fission is likely to be more important in their study and, on the other hand, and probably of more significance, the product expected to be formed initially in their study would be 1,3-dimethoxy-2-methylprop-1-ene. This molecule would be expected to decompose rapidly at the temperatures in question *via* a sequence of two retro-ene reactions and give eventually 2-methyl-1-propene and two molecules of methanal (see scheme 5).

$$\overline{MeOCHCHMeCHOMe} \longrightarrow MeOCH_2CMe{=}CHOMe$$

$$MeOCH_2CMe{=}CHOMe \longrightarrow CH_2{=}CHMeCH_2OMe + CH_2O$$

$$CH_2{=}CHMeCH_2OMe \longrightarrow Me_2C{=}CH_2 + CH_2O$$

SCHEME 5

APPENDIX

The following reaction sequence, in which all reactions are first order, was assumed for the decomposition of methoxycyclopropane.
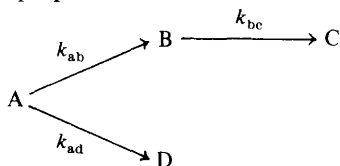
Hence
$$[A]_t = [A]_0 \exp\left[-(k_{ab}+k_{ad})\,t\right]$$

and
$$d[B]/dt = k_{ab}[A] - k_{bc}[B].$$

Integrating from time $= 0$ to t, and assuming $[B]_0 = 0$, gives

$$\frac{[B]}{[A]_0 - [A]_t} = \frac{k_{ab}}{k_{ab}+k_{ad}} - \frac{k_{bc}\displaystyle\int_0^t [B]\,dt}{[A]_0 - [A]_t}. \tag{1}$$

In the present study $k_{ab}+k_{ad}$ represent the sum of the rate constants for loss of methoxy-cyclopropane and $[B]$ represents the concentration of either (Z)-1-methoxyprop-1-ene or 3-methoxyprop-1-ene. The integral in eqn (1) was obtained graphically and a plot made of the l.h.s. of eqn (1) against

$$\int_0^t [B]\,dt/([A]_0 - [A]_t).$$

This plot proved to be linear and k_{bc} and $k_{ab}/(k_{ab}+k_{ad})$ were determined from the slope and intercept of this plot. This method proved a much simpler method to obtain the rate constants than fitting the data to the explicit form of the integrated rate equation for B.

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