J. Chem. Soc., Faraday Trans. 1, 1985, **81**, 1415–1424

Kinetics of the Gas-phase Thermal Decompositions of 1-Methoxy-1-methylcyclopropane and *cis*- and *trans*-1-Methoxy-2-methylcyclopropane

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Received 25*th July*, 1984

In the temperature range 665–737 K the thermal decomposition of 1-methoxy-1-methylcyclopropane follows first-order kinetics with a rate constant given by the equation

$$k/\mathrm{s}^{-1} = 10^{14.76\pm0.81}\exp(-252\pm10\ \mathrm{kJ\ mol^{-1}}/RT).$$

The presence of the 1-methyl substituent destabilises the transition state for reaction. Secondary decomposition of the initially formed isomeric products precludes the determination of their individual rates of formation.

Cis- and *trans*-1-methoxy-2-methylcyclopropane undergo first-order, reversible, geometric isomerisation in competition with structural isomerisation to give *cis*- and *trans*-1-methoxybut-1-ene and 1-methoxy-2-methylpropene in the temperature range 597–689 K:

$$k_{cis\rightarrow trans}/\mathrm{s}^{-1} = 10^{15.25\pm0.23}\exp(-235.4\pm2.8\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{trans\rightarrow cis}/\mathrm{s}^{-1} = 10^{14.99\pm0.80}\exp(-233.7\pm9.9\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{cis\rightarrow cis\text{-1-methoxybut-1-ene}}/\mathrm{s}^{-1} = 10^{13.79\pm0.29}\exp(-233.1\pm3.6\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{cis\rightarrow trans\text{-1-methoxybut-1-ene}}/\mathrm{s}^{-1} = 10^{13.29\pm0.66}\exp(-234.4\pm8.1\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{cis\rightarrow \text{1-methoxy-2-methylpropene}}/\mathrm{s}^{-1} = 10^{12.4\pm1.0}\exp(-225\pm12\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{trans\rightarrow cis\text{-1-methoxybut-1-ene}}/\mathrm{s}^{-1} = 10^{14.05\pm0.62}\exp(-243.7\pm7.8\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{trans\rightarrow trans\text{-1-methoxybut-1-ene}}/\mathrm{s}^{-1} = 10^{13.0\pm0.9}\exp(-233\pm11\ \mathrm{kJ\ mol^{-1}}/RT)$$
$$k_{trans\rightarrow \text{1-methoxy-2-methylpropane}}/\mathrm{s}^{-1} = 10^{13.5\pm1.0}\exp(-235\pm13\ \mathrm{kJ\ mol^{-1}}/RT).$$

On the basis of a biradical mechanism the results provide evidence for the formation of distinguishable biradicals on opening the *cis*- and *trans*-1-methoxy-2-methylcyclopropane ring. Estimates are made of the relative rates of ring closing, internal rotation and hydrogen-atom transfer of the biradicals.

We have previously reported a study of the gas-phase thermal decomposition of methoxycyclopropane.[1] The methoxy group increased the reaction rate and lowered the activation energy for structural isomerisation by *ca.* 45 kJ mol^{-1} compared with the value for cyclopropane. The transition state and biradical formed were envisaged to be resonance stabilised through participation of the oxygen-atom lone pair of electrons and to have some resultant ionic character. Structural isomerisation occurred by hydrogen-atom transfer in the biradical. Using scheme 1, the measured rate constant can be equated to $k_r k_h/(k_{-r}+k_h)$. It was thought that for methoxycyclopropane $k_h \gg k_{-r}$, whereas for alkylcyclopropanes it is believed that $k_h \ll k_{-r}$.

Scheme 1.

In order to investigate further the mechanism of this reaction we have studied the kinetics of the gas-phase reactions of 1-methoxy-1-methylcyclopropane (1MMC) and *cis*- and *trans*-1-methoxy-2-methylcyclopropane (*c*MMC and *t*MMC).

EXPERIMENTAL

All thermal kinetic studies were carried out as previously described[2] in a conventional 'static' system using Pyrex reaction vessels aged by pyrolysis of *ca.* 20 Torr† hexamethyldisiloxane at 798 K 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} and the other was of similar external dimensions but was not packed ($S/V = 1$ cm^{-1}, volume *ca.* 150 cm^3). Young's PTFE barrel, greaseless stopcocks were used in all parts of the vacuum system in contact with pyrolysed material.

Analyses were carried out on a Perkin-Elmer 452 gas chromatograph using a 50 m squalane SCOT column at *ca.* 15 °C with helium carrier gas and flame ionisation detection (f.i.d.). F.i.d. sensitivity coefficients for all compounds were assumed to be directly proportional to carbon number. Peak areas were determined using an LDC 308 computing integrator. Products were identified by gas-chromatographic retention time and by g.l.c./mass spectrometry (Kratos MS 30 mass spectrometer).

1MMC, *c*MMC and *t*MMC were prepared by the reaction of methylene iodide with the appropriate methoxypropene in the presence of a zinc–copper couple[3] and 1,2-dimethoxyethane.[4] In the absence of 1,2-dimethoxyethane low yields of the required cyclopropane were obtained. The products were purified, first by fractional distillation on a 0.6 m Podbielniak column and then by preparative gas chromatography. Final product purities were 1MMC (b.p. 60 °C) 99.7% (0.2% 2-methoxypropene), *c*MMC (b.p. 69 °C) 99.4% (0.2% *t*MMC, 0.3% *cis*-1-methoxyprop-1-ene) and *t*MMC (b.p. 65 °C) 94.4% (0.4% *c*MMC, 0.2% diethyl ether, 4.9% an unidentified C_5 vinyl or allyl ether not formed as a reaction product in kinetic studies). The identities of the products were confirmed by n.m.r. 3-Methoxybut-1-ene was prepared by the action of methyl iodide on the sodium salt of 3-hydroxybut-1-ene.[5] Other methoxypropenes and methoxybutenes used in the study for kinetic, synthetic or identification purposes were prepared by the elimination of methanol from the appropriate acetal.[6, 7]

RESULTS

1-METHOXY-1-METHYLCYCLOPROPANE

The kinetics of the thermal decomposition of 1MMC were investigated in the temperature range 665–737 K at up to 20% decomposition. The results showed that 3-methoxybut-1-ene and (*E*)- and (*Z*)-2-methoxybut-2-ene, the expected isomeric reaction products, were formed in rather small amounts together with very much larger amounts of other molecules that had clearly been formed as the result of fragmentation reactions. The extent of the fragmentation was such that at 18% decomposition the isomeric products constituted *ca.* 1.3% of that total, *i.e.* they accounted for only *ca.* 7% of the reactant decomposed. Methane, ethane, propane, but-1-ene and *cis*- and *trans*-but-2-ene formed *ca.* 75% of the fragmentation products.

Separate pyrolyses of 20 Torr 3-methoxybut-1-ene and a mixture of (*E*)- and (*Z*)-2-methoxybut-2-ene with 2-methoxybut-1-ene at 702 K for 31 min (this time would have resulted in *ca.* 25% decomposition of 1MMC) produced *ca.* 95% decomposition of these molecules to mainly hydrocarbon products (methanol, carbon monoxide, water *etc.* would not have been detected). Scheme 2 summarises the observed reactions.

Because of the rapid decomposition of the initial reaction products it was clear that

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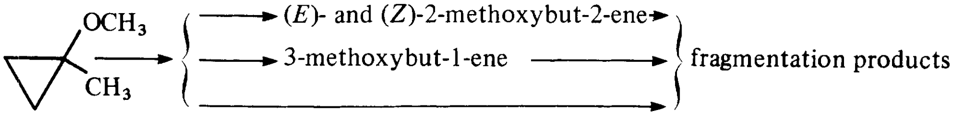
† 1 Torr = 133 N m^{-2}.



Scheme 2.

Table 1. First-order rate constants for the thermal decomposition of 1-methoxy-1-methylcyclopropane

T/K	$k/10^{-5}\ \mathrm{s}^{-1}$
737.1	83
729.1	55
717.2	27
709.1	18
693.4	5.8
666.1	0.95
649.7	0.37

accurate determination of the rate constants for the formation of these products from 1MMC would not be possible and it was therefore decided only to determine the overall rate of loss of 1MMC; this proved to be a first-order process on the basis of the time dependence. First-order rate constants were determined at 7 temperatures using 28 Torr initial reactant and they are listed in table 1. In Arrhenius form they are given by the equation

$$k/\mathrm{s}^{-1} = 10^{14.76\pm0.81}\exp(-251.7\pm10.4\ \mathrm{kJ\ mol^{-1}}/\boldsymbol{R}T).$$

All error limits quoted in this paper are statistical 95% certainty limits.

cis- AND *trans*-1-METHOXY-2-METHYLCYCLOPROPANE

The kinetics of the thermal decomposition of *c*MMC and *t*MMC were investigated in the temperature range 597–689 K. The initial reactant underwent a reversible, first-order (on the basis of time and pressure dependence), geometric isomerisation in competition with structural isomerisation and some fragmentation reactions. The structural isomerisation products were identified as *cis*- and *trans*-1-methoxybut-1-ene and 1-methoxy-2-methylpropene. No 3-methoxy-2-methylpropene or 1-methoxybut-2-ene were detected; however, if these allylic ethers were formed in the same ratio to the vinylic ethers as observed from methoxycyclopropane[1] then, under the conditions used, they would not have been detected. Methane, ethane, propane, butenes and pentenes were identified as the major fragmentation products although they were not formed in quite the same proportions from *c*MMC and *t*MMC. The fragmentation products constituted < 9% of the total decomposition products under the conditions used. No structural isomers were detected that would have resulted from the cleavage of the carbon–carbon bond of the cyclopropane ring opposite to the methoxy substituent, *i.e.* the C(2)—C(3) bond.

Scheme 3 summarises the various channels for the reaction of *c*MMC and *t*MMC.

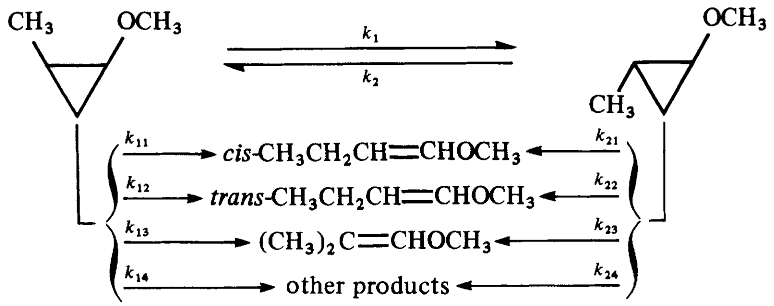
Variation of the initial pressure of reactant between 5 and 88 Torr at 690 K produced no change in the fractional rates of formation of any isomerisation products.

Secondary decomposition of the initially formed structural isomers proved significant at high percentage conversions and hence the majority of runs used to determine rate

Table 2. Rate constants for reactions of *cis*- and *trans*-1-methoxy-2-methylcyclopropane for 28 Torr initial reactant pressure[a]

T/K	rate constants/10^{-6} s^{-1}									
	k_1	k_2	Σk_{1i}	k_{11}	k_{12}	k_{13}	Σk_{2i}	k_{21}	k_{22}	k_{23}
689.8	2630	1900	500	140 (4)	38.0 (3)	19.0 (4)	220	45 (3)	25 (3)	40 (1)
674.4	1070	768	200	55 (3)	15.0 (3)	8.50 (4)	83	14.3 (5)	9.5 (2)	20 (2)
657.8	350	273	65	17.8 (4)	3.86 (4)	2.52 (1)	24	4.5 (3)	3.0 (2)	7.0 (3)
643.3	140	107	27	8.25 (4)	1.95 (5)	1.15 (5)	12	1.8 (3)	1.0 (2)	2.8 (1)
625.8	39.6	28.9	6.7	2.17 (4)	0.53 (3)	—	—	0.83[b]	0.41 (3)	1.3[b]
613.2	15.9	15.6[b]	2.9	0.89 (5)	0.18 (2)	—	1.7	0.22 (2)	0.15 (2)	0.25 (2)
597.3	4.6	4.9[b]	0.66	0.24 (2)	0.07 (3)	—	0.59	0.053 (1)	—	0.096 (1)

[a] Weighting factors used for the determination of Arrhenius parameters are shown in parentheses. [b] These data deviated considerably from the best straight line through the data points and were not used in determining the quoted Arrhenius parameters.



Scheme 3.

Table 3. Arrhenius parameters for the reactions of *cis*- and *trans*-1-methoxy-2-methylcyclopropane

reactant	product	rate constant	$\log A/\mathrm{s}^{-1}$	$E_a/\mathrm{kJ\ mol^{-1}}$
*c*MMC	*t*MMC	k_1	15.25 ± 0.23	235.4 ± 2.8
*t*MMC	*c*MMC	k_2	14.99 ± 0.80	233.7 ± 9.9
*c*MMC	*cis*-1-methoxybut-1-ene	k_{11}	13.79 ± 0.29	233.1 ± 3.6
*c*MMC	*trans*-1-methoxybut-1-ene	k_{12}	13.29 ± 0.66	234.4 ± 8.1
*c*MMC	1-methoxy-2-methylpropene	k_{13}	12.4 ± 1.0	225 ± 12
*t*MMC	*cis*-1-methoxybut-1-ene	k_{21}	14.05 ± 0.62	243.7 ± 7.8
*t*MMC	*trans*-1-methoxybut-1-ene	k_{22}	13.0 ± 0.9	233 ± 11
*t*MMC	1-methoxy-2-methylpropene	k_{23}	13.5 ± 1.0	235 ± 13

constants were limited to < 15% reaction. At seven temperatures, with 28 Torr initial reactant, estimates of $k_1 + \Sigma k_{1i}$ and $k_2 + \Sigma k_{2i}$ were obtained from the slopes of the first-order rate plots for loss of initial reactant. Estimates of Σk_{1i} and Σk_{2i} were deduced from the initial rates of formation of all products other than the geometric isomer. These values were then used as the input values for a Simplex non-linear least-squares program,[8] which utilised the experimental data from both *c*MMC and *t*MMC, as initial reactants at the same temperature, to obtain the best estimates for k_1, k_2, Σk_{1i} and Σk_{2i}. Partition of Σk_{1i} and Σk_{2i} into the values for the individual rate constants was carried out using the initial slopes of plots of percentage of the relevant reaction product against percentage total reaction. The rate constants so determined are listed in table 2 and the Arrhenius parameters derived from them are reported in table 3. The Arrhenius parameters quoted for the structural isomerisation used a weighted least-squares procedure in which the weighting factors were based on the number of data points available to determine the separate rate constants.

Some runs were undertaken at 657, 674 and 689 K in an attempt to determine directly the equilibrium constant for the geometric isomerisation, by pyrolysing *c*MMC for long times. The ratio of *t*MMC to *c*MMC passed through a rather flat maximum of *ca.* 1.60 at *ca.* 40% decomposition of *c*MMC + *t*MMC to structural isomers and fragmentation products, instead of reaching a constant value. It seems likely that a secondary reaction product was contributing to the *c*MMC peak at high percentage reaction and so further attempts to determine the equilibrium constant directly were not made and these data were not used in the determination of the quoted rate constants.

Studies of the rates of reaction of *c*MMC at 675 K in the packed reaction vessel gave results identical to those that had been obtained in the unpacked vessel. Because of lack of reactant only one run was carried out in the presence of nitric oxide. Addition of 10% nitric oxide to *c*MMC at 690 K did not affect the rate of geometric isomerisation but reduced the rates of formation of fragmentation products by *ca.* 50% and also slightly reduced the rates of formation of structural isomerisation products. It is thus possible that our measured rates for structural isomerisation do have some contribution from radical pathways, although it is unlikely that this contribution is significant.

DISCUSSION

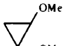
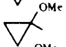
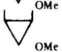
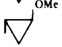
A biradical mechanism has been used to explain the thermal unimolecular rearrangements of cyclopropanes and this mechanism proved capable of explaining the reaction products and the observed parameters for the thermal decomposition of methoxycyclopropane.

The studies reported here on *c*MMC and *t*MMC indicate that the major processes are homogeneous and probably unimolecular and so also might be expected to proceed *via* a similar mechanism. Data for 1MMC indicate a first-order reaction but the measured rate constants can only be considered to represent the maximum values for the unimolecular structural isomerisation.

Table 4 lists the rate constants for structural isomerisation of some cyclopropanes bearing alkyl and/or methoxy substituents. For alkyl-substituted cyclopropanes the reaction rate increases slightly from cyclopropane to methylcyclopropane to 1,1-dimethylcyclopropane, whereas comparison of the total reaction rates for methoxycyclopropane and 1MMC shows that the addition of the 1-methyl substituent reduces the reaction rate significantly. This effect is entirely in accord with the biradical mechanism above, as the consequence of attaching the electron-donating methyl group to the partially negatively charged carbon atom is to reduce the resonance stabilisation caused by the methoxy group in the transition state for hydrogen-atom transfer and hence to slow the reaction rate. The observation[9] that the activation energy for the isomerisation of 1-methoxy-1-vinylcyclopropane to 1-methoxycyclopentene is only *ca.* 21 kJ mol^{-1} below the activation energy for the corresponding reaction of vinylcyclopropane, whereas the reduction in activation energy is *ca.* 46 kJ mol^{-1} for the isomerisation of 1-methoxy-2-vinylcyclopropane, is presumably the consequence of similar counter-stabilising effects of the vinyl and methoxy groups when they are attached to the same carbon atom. Analogously, in studies of the differences in the heats of formation of various vinyl ethers, Taskinen[7, 10] has observed that a methyl group β to the methoxy group has a less stabilising effect by *ca.* 7 kJ mol^{-1} than is observed in the equivalent alkenes.

Comparison of the rates of structural isomerisation of 1,2-disubstituted cyclopropanes given in table 4 shows that the presence of a methyl group at the 2 position has very similar effects in most instances for both methyl- and methoxy-substituted cyclopropanes. In both systems the rates of geometric isomerisation are much faster than the rates of structural isomerisation and the A factors for geometric isomerisation are identical within experimental error. It is clear therefore that our previous contention[1] that $k_h \gg k_{-r}$ is not tenable for 1-methoxy-2-methylcyclopropane (MMC) and estimates of k_{-r}/k_h are made in the Appendix. Thus the stabilisation energies for the methoxy substituent in our earlier paper refer to the transition states for hydrogen-atom transfer rather than to the initial ring opening. Comparison of the Arrhenius parameters for geometric isomerisation of MMC and 1,2-dimethylcyclo-

Table 4. Rate constants at 665 K for the gas-phase thermal decomposition of some substituted cyclopropanes [C(1)—C(2) or C(1)—C(3) bond fission as marked]

cyclopropanes			methoxycyclopropanes			
reactant	k(structural isomerisation) $/10^{-6}\ s^{-1}$	ref.	reactant	k(total) $/10^{-6}$ s	k(structural isomerisation) $/10^{-6}\ s^{-1}$	ref.
	0.8	*a*				
	1.2	*b*		41	33	1
	3.0	*c*		10	—	this work
	1.3, C(1)—C(2) 0.8, C(1)—C(3)	*d*		110	39, C(1)—C(2) 5, C(1)—C(3)	this work
	0.7, C(1)—C(2) 0.8, C(1)—C(3)	*d*		47	14, C(1)—C(2) 11, C(1)—C(3)	this work

[a] W. E. Falconer, T. F. Hunter and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 609. [b] D. W. Placzek and B. S. Rabinovitch, *J. Chem. Phys.*, 1965, **69**, 2141; D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 1964, **86**, 564. [c] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1959, 3953. [d] M. C. Flowers and H. M. Frey, *Proc. R. Soc. London, Ser. A*, 1960, **257**, 122; 1961, **260**, 424.

propane suggests that stabilisation energy from the methoxy substituent in respect of the ring-opening reaction may be no more than 13 kJ mol^{-1}.

The error limits of the Arrhenius parameters do not allow an assessment of whether or not it is energetically easier to break the C(1)—C(2) or the C(1)—C(3) bond of MMC. However, it is clear that the rates of formation of products resulting from C(1)—C(2) rupture is greater than for C(1)—C(3) rupture and the rates are greatest from the *cis* isomer; these observations are all also true for 1,2-dimethylcyclopropane. Estimates of the relative rates of breaking C(1)—C(2) and C(1)—C(3) bonds can be obtained using the detailed mechanism shown in the Appendix. For C(1)—C(3) bond rupture *t*MMC reacts faster than *c*MMC, in contrast to 1,2-dimethylcyclopropane for which the rates are the same from both isomers. This difference is presumably a consequence of the details of the relative rates of all the elementary reactions involved, *i.e.* the relative rates of ring opening and ring closing, internal rotation and hydrogen-atom transfers in the biradicals.

Lustgarten and Richey,[11] in a study of the isomerisation of 7-alkoxybicyclo[2.1.1]-heptadienes to cycloheptatrienes, also found that the alkoxy group had large accelerating effects on the reaction rates. They considered that the most likely reaction path involved a biradical and considered a zwitterionic intermediate unlikely in the light of a small solvent effect. Although we do find evidence, from the effect of a 1-methyl substituent, to support a partial negative charge residing on the radical centre immediately bonded to the oxygen, the lack of effect of the 2-methyl substituent also suggests that the other radical centre is not charged.

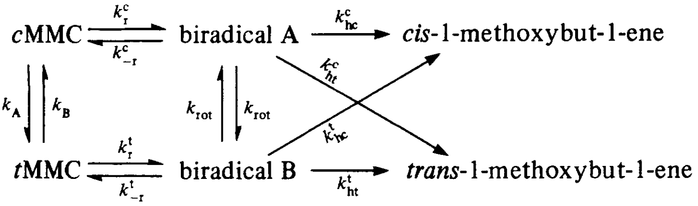
Kirmse and Zeppenfeld[12] determined the rate constants and Arrhenius parameters for the interconversion of the geometric isomers of 1,2-dimethoxy-3-methylcyclopropane and a rate constant of 3.6×10^{-7} s^{-1} at 288 °C for the conversion of *cis*-1-methoxy-*cis*-2,3-dimethylcyclopropane into its geometric isomers. At 288 °C we calculate that the rate constant for conversion of *c*MMC into *t*MMC would have been 2.3×10^{-7} s^{-1}, *i.e.* essentially the same value bearing in mind the combined uncertainties. Kirmse and Zeppenfeld deduced from their data that there was no preference for a synchronous double rotation, rather than a single rotation, mechanism. Our data also have information pertinent to this as a consequence of an important difference that exists between reactions of 1,2-dimethylcyclopropane and MMC.

The ratios of the rates of formation of 2-methylbut-2-ene to 2-methylbut-1-ene and of *cis*-pent-2-ene to *trans*-pent-2-ene are essentially the same from both *cis*- and *trans*-1,2-dimethylcyclopropane. Thus for this reaction no conclusions can be drawn as to whether or not distinct and different biradicals are formed when opening the cyclopropane ring of the two different geometric isomers. However, in the current study the ratio of *cis*- to *trans*-1-methoxybut-1-ene is *ca.* 4.1 from *c*MMC and *ca.* 1.6 from *t*MMC. Hence if a biradical mechanism is assumed, different biradicals must be formed from the two isomers on breaking the C(1)—C(2) bond. A concerted, conrotatory (or disrotatory) ring-opening reaction would be consistent with this observation, though it is not a requirement. Concerted ring opening and ring closing would necessitate that the geometric isomerisation occurred as the consequence of breaking the C(1)—C(3) bond as no geometric isomerisation can occur for a concerted opening at the C(1)—C(2) bond. Thus the geometric isomerisation would be in competition with isomerisation to 1-methoxy-2-methylpropene. However, based on the work of Kirmse and Zeppenfeld[12] and on other cyclopropane studies (*e.g.* the geometric isomerisation and racemisation of 1-ethyl-2-methylcyclopropane[13]), we feel that the predominant ring-opening reaction is not concerted and that the geometric isomerisation is a consequence of a biradical mechanism in which either the C(1)—C(2) or the C(1)—C(3) bond has been ruptured. From our data, estimates of the various elementary processes involved may then be obtained based on some reasonable assumptions (see the Appendix). The general conclusions are that (*a*) the *c*MMC ring opens at C(1)—C(2) up to three times faster than *t*MMC, (*b*) hydrogen-atom transfer in the biradicals is significantly slower (> 30 times) than either internal rotation or ring closure and (*c*) the ratio of $k_{\text{cyclisation}}$ to $k_{\text{internal rotation}}$ is *ca.* 1. These are very similar conclusions to those that may be drawn from alkylcyclopropane studies[13] with perhaps a slight reduction in the rates of internal rotation relative to cyclisation (*cf.* $k_{\text{cyc}}/k_{\text{rot}} = 0.2$ for 1-ethyl-2-methylcyclopropane[13]) from that expected, bearing in mind the similar relative size of the rotors.

We thank Prof. H. M. Frey for the Simplex computer programme used to derive the rate constants from the experimental data and I. A. A. thanks the Government of Pakistan for the award of a scholarship.

APPENDIX

Scheme 4 represents the detailed biradical mechanism for the geometric isomerisation of, and for the formation of *cis*- and *trans*-1-methoxybut-1-ene from, MMC. All rate constants with lower case subscripts are rate constants for elementary processes. Rate constants k_A and k_B represent the overall rates of geometric isomerisation *via* C(1)—C(3) bond rupture. Biradicals A and B are formed by C(1)—C(2) bond rupture in *c*MMC and *t*MMC, respectively.



Scheme 4.

In order to derive expressions for the relative rate constants for the various elementary processes occurring, an initial simplifying assumption is necessary. We have chosen to assume that the rates of internal rotation of the two biradicals are the same. Using this, and the steady-state assumption for biradical concentrations, leads to the following equations for relative rate constants in terms of the measured rate constants defined in scheme 3.

$$\frac{k^c_{-r}}{k^c_{hc}} = \frac{k_2(1-\alpha\beta)}{(1+\delta)(k_{21}-\beta k_{22})}$$

$$\frac{k^t_{-r}}{k^t_{ht}} = \frac{k_1(1-\alpha\beta)}{(1+\delta)(k_{12}-\alpha k_{11})}$$

$$\frac{k^c_r}{k^t_r} = \frac{k_1 k^c_{-r}}{k_2 k^t_{-r}}$$

$$\frac{k^c_{hc}}{k^t_{ht}} = \frac{[(1+\delta)(k_{12}+k_{11})+k_1](k_{21}+\beta k_{22})+k_2(k_{11}-\beta k_{12})}{[(1+\delta)(k_{21}+k_{22})+k_2)](k_{12}-\alpha k_{11})+k_1(k_{22}-\alpha k_{21})}$$

$$\frac{k_{rot}}{k^t_{ht}} = \frac{k^c_{hc}[(1+\beta)(k_{12}-\alpha k_{11})+k_1(1-\alpha\beta)/(1+\delta)]}{k^t_{ht}[k_{11}-\beta k_{12}-k^c_{hc}(k_{12}-\alpha k_{11})/k^t_{ht}]}$$

where $\alpha = k^c_{ht}/k^c_{hc}, \quad \beta = k^t_{hc}/k^t_{ht}, \quad \delta = k_A\gamma/(k^c_r k_{rot} k^t_{-r})$

and $\gamma = (k^c_{-r}+k_{rot}+k^c_{hc}+k^c_{ht})(k^t_{-r}+k^t_{hc}+k^t_{ht})+k_{rot}(k^c_{-r}+k^c_{hc}+k^c_{ht}).$

Table 5. Calculated rate-constant ratios based on rate-constant data at 643 K

assumed values	α	0	0	0.2	0.2	0.2	0	0.2
	β	0	0	0.2	0.2	1	0.2	0
	δ	0	1	0	1	1	1	1
k^{c}_{-r}/k^{c}_{hc}		57	28	63	32	73	33	28
k^{t}_{-r}/k^{t}_{ht}		76	38	374	188	156	38	195
k^{c}_{hc}/k^{t}_{ht}		2.8	2.8	5.9	6.0	4.1	2.6	6.4
k^{c}_{-r}/k_{rot}		0.9	0.9	2.3	2.3	5.4	1.0	2.1
k^{t}_{-r}/k_{rot}		0.4	0.4	2.3	2.3	2.8	0.5	2.2
k^{c}_{r}/k^{t}_{r}		2.8	2.8	1.3	1.3	2.5	3.0	1.2

δ represents the rate of geometric isomerisation *via* C(1)—C(3) bond rupture relative to a rate *via* C(1)—C(2) bond rupture equal to unity.

Using rate constants calculated at 643 K from the Arrhenius parameters, the relative rate constants for the elementary processes are given in table 5 for assumed values of α, β and δ. For consistency with the experimental data α must be < 0.25 and $\beta < 1.45$.

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