

Kinetics of the Gas-phase Thermal Decomposition of Methylcyclopropanemethanol

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Summary: Kinetics of the gas phase thermal decomposition of methylcyclopropanemethanol (MCM) was studied over the temperature range 640-720 K and pressure between 4-16 torr using static system. Initial runs carried out in aged unpacked reaction vessel yield small amount of expected isomerization products i.e. cis and trans-2-methyl-1-buten-4-ol and 2-methyl-2-buten-1-ol. Formed simultaneously with the isomeric products were large amounts of other products that have clearly formed as the result of fragmentation reactions. In view of the complexities due to rapid secondary decomposition of initial reaction products it was decided only to determine the overall rate of loss of methylcyclopropane methanol; this proved to be a first order, homogenous, unaffected by the addition of nitric acid and probably unimolecular. First order rate constants were determined at six temperatures using 15 torr initial reactant. The Arrhenius parameters are given in the rate equation

$$k_{\text{total}}/\text{s}^{-1} = 10^{14.8 \pm 1.7} \exp(-248.2 \pm 12.1 \text{ kJ mol}^{-1}/RT)$$

The results are compared with those for other cyclopropanes and the mechanism considered likely to involve a biradical transition state.

Introduction

Among unimolecular reactions, the gas phase thermal isomerization of cyclopropane and its derivatives have assumed a central role in the field of reaction kinetics due to their frequent use as models for the testing of various theories of unimolecular reactions [1-5]. Thermal studies of alkyl, vinyl [6], phenyl [7], vinyl [8], cyano [9] and methoxy [10] substituted cyclopropane all have been explained in term of biradical mechanism. The observed Arrhenius parameters are consistent with the stabilization effects, which these substituents gives to the radical centers.

No previous work has been reported on the decomposition of cyclopropane substituted with -CH₂OH group. It is therefore of interest to determine whether such compounds exhibits the same type of behavior as those previously determined. Present study is also a part of an investigation to add to existing experimental data for cyclopropane thermolysis and to further knowledge in this respect.

Result and Discussion

Kinetics of the thermal gas phase decomposition of methylcyclopropane methanol [MCM] were investigated in the temperature range 640-720 K, in

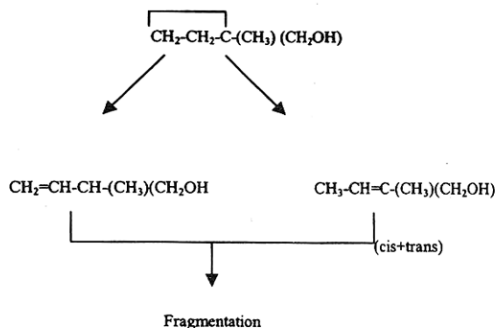
an aged unpacked reaction vessel and found to occur according to the reaction scheme-1.

Due to the rapid secondary decomposition of isomeric products it was not possible to evaluate the rate constants for the formation of individual products. Therefore, the kinetics parameters reported were based on the total loss of the reactant. First order rate plots for the loss of the initial reactant (15 Torr initial reactant pressure) were linear as shown in Fig 1. The decomposition rate constant (k_{total}) was calculated from the initial slope of this plot. The rate constants so determined are listed in Table 1. The following Arrhenius parameters were obtained from these rate constants:

$$k_{\text{(MCM} \rightarrow \text{Product)}}/\text{s}^{-1} = 10^{14.8 \pm 1.7} \exp(-248.19 \pm 12.1 \text{ kJ mol}^{-1}/RT)$$

The error limits quoted are statistical 95 % certainty limits. Arrhenius plot for the loss MCM is shown in Fig. 3. The Arrhenius parameters were determined by a linear, non weighted least square procedure [11]. The Arrhenius parameters obtained are similar to those found for cyclopropane and alkyl and methoxycyclopropanes (Table 3). The most likely mechanism for the decomposition of MCM by analogy to that proposed for other substituted cyclopropanes could be a two step process involving the

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Scheme 1

Table-1: Rate Constants for the Decomposition of Methylcyclopropane Methanol with an Initial Pressure of 15 torr in Unpacked Vessel

Temperature K	$k_{\text{total}}/10^{-6} \text{ s}^{-1}$
720	350
710	550
702	204
694	127
680	51.5
673	29.3
660	11.6
648	5.67
640	3.70

Table-2: Pressure Dependence of the First Order Rate Constant for the Overall Decomposition of MCM at 660 K for 15 Minutes Kinetics Runs

Total Pressure/Torr	$k_{\text{total}}/10^{-5} \text{ s}^{-1}$
16	1.17
12	1.16
10	1.16
8	1.14
9	1.12
4	1.12

Table-3: Rate constant for 665 K for the Gas Phase Thermal Decomposition of Some Substituted Cyclopropanes.

Reactant	$k(\text{total})/10^{-6}$	$\log A/\text{s}^{-1}$	$E_a \text{ KJ/mole}$	Ref
Cyclopropane	0.8	15.5	272.0	14
Methylcyclopropane	1.2	14.8	260.7	7
Methoxycyclopropane	41	14.04	243.0	11
1-methoxy-1-methyl cyclopropane	10	14.76	251.7	15
1-methylcyclopropanemethanol	20	14.8	248.2	This work

formation of biradical by breaking C1-C2 carbon bond or C1-C3 carbon bonds followed by vicinal H atom transfer as shown in scheme-2.

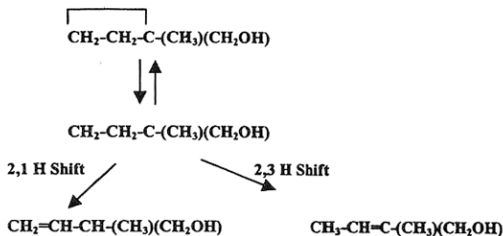
The pressure dependence on the reaction was investigated between 4 and 16 torr at 522 K for 15 minutes pyrolysis time. The results are shown in (Figure 3) and Table (2). Total decomposition showed a small decrease with decreased in pressure. This could be due to normal unimolecular fall off. However, as the effect of pressure was small no correction to the Arrhenius parameters was attempted.

The effect of surface on the reaction was studied at 652 K using "aged" packed reaction vessel with 10 Torr initial reactant pressure. It was found that the overall reaction rate was 15 % faster in packed reaction vessel than in unpacked reaction vessel. Evidently, there is some surface effect but assuming the extent of this reaction is proportional to the S/V ratio for the reaction vessels, the surface reaction constitute only 1.2 % of the overall reaction rate in unpacked vessel.

The effect of nitric oxide on the reaction was investigated at 650 K using 10 % nitric oxide added to initial reactant. The overall reaction rate was unaffected indicating the isomerization products were almost certainly formed by unimolecular, non-radical pathways.

Experimental

All thermal kinetics studies were carried out as previously described [12] in a conventional static system using pyrex reaction vessels which were aged by the pyrolysis of ca. 20 torr hexamethyldisiloxane at 512 °C for 48 hours. Two reaction vessels were employed; one was packed with short lengths of



Scheme 2

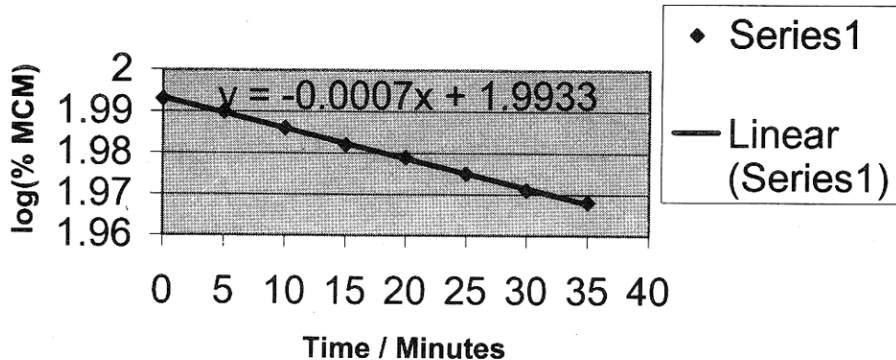


Fig. 1: First Order Rate Plot for the Loss of MCM at 660 K (15 torr initial pressure)

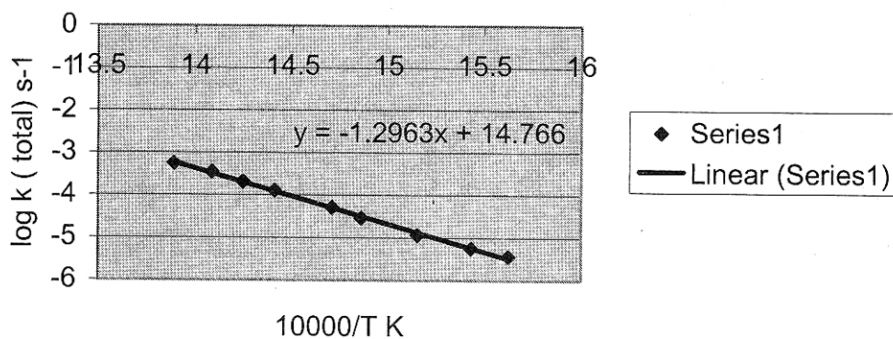


Fig. 2: Arrhenius plot for the decomposition of MCM

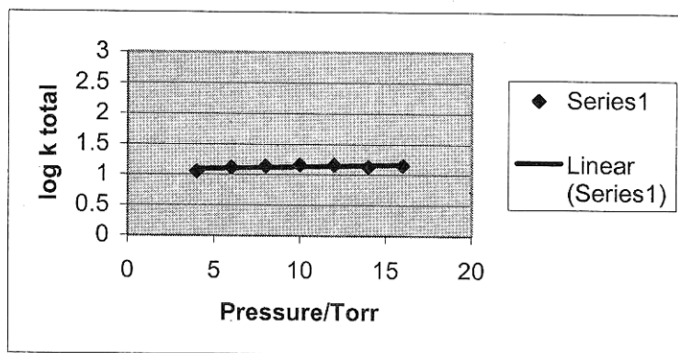


Fig. 3: Pressure dependence of rate constant for the decomposition of MCM at 660 K.

pyrex tubing to give surface to volume ratio (S/V) of ca. 12 cm^{-1} , the other was of similar dimensions but was not packed (S/V ca. 1 cm^{-1} , volume 150 cm^3). Young's greaseless stopcocks were used in all parts of the vacuum system associated with the pyrolysis and with the analysis of pyrolyzed material. Reaction vessels were immersed in a fused salt ($\text{NaNO}_3/\text{NaNO}_2/\text{KNO}_3$ ternary eutectic) thermostat, the temperature was maintained to $\pm 0.1^\circ\text{C}$ by ADP 5 temperature controller. Temperature was measured with a resistant thermometer. Dead space of the reaction was 0.5 % and was ignored in the calculations.

Analysis were carried out on a Shimadzu GC 7AG gas chromatograph using $30\text{m} \times 0.25 \text{ mm}$ Squalane WCOT maintained at room temperature with nitrogen carrier gas. Flame ionization detector coupled to a wide range of amplifier and Spectra Physics model SP 4600 data jet integrator were used for the quantitative estimation of the eluted products. Products were identified by gas chromatographic retention times.

Methylcyclopropane methanol was purchased from Aldrich company (USA) was 98 % pure and used without further purification.

References

1. K. A. Holbrook, M. J. Pilling and S. H. Robertson, "Unimolecular Reactions" John Wiley (1996).
2. P.J.Robinson and K.A.Halobrook, "Unimolecular Reactions" Wiley, London (1972).
3. W.Frost, "Theory of Unimolecular Reactions" Academic Press, New York,(1973).
4. Rosana M. Romano, Carlos O. Della Vedova, Joanna Czarnowski, *Intl. J. Chem. Kinet.*, **35**, 532 (2003).
5. G. Huybrechts and G. Wouters, *Int. J. Chem. Kinet.*, **34**, 316 (2002).
6. Sandrina Coquet and Parisa A. Ariya, *Int. J. Chem. Kinet.*, **32**, 478 (2000).
7. a) M.C.Flowers and H.M.Frey, *J.Chem.Soc.*, 3953 (1959). b)M.C.Flowers and H.M.Frey, *Proc. Roy. Soc.*, A257, 122 (1960). c) H.M. Frey and D.C.Marshall, *J.Chem.Soc.*, 5717 (1963) d) C.S.Elliot and H.M.Frey, *J.Chem.Soc.*, 900 (1964).
8. a) M.C.Flowers and H.M.Frey, *J.Chem.Soc.*, 3547 (1961). b) C.A. Wellington, *J.Phy.Chem.*, **66**, 1671 (1962)
9. a) R.J.Crawford and T.R. Lynch, *Can. J.Chem.*, **46**, 1457 (1968). b) L. B. Rodewald and C. H. Depuy, *Tetrahedron Letter*, 2951 (1964).
10. J. E. Baldin and C.G. Carter, *J.Am.Chem.Soc.*, **100**, 3942 (1978); **101**, 1325 (1979).
11. Iftikhar A. Awan and M.C. Flowers, *J.Chem.Soc., Faraday Trans. 1*, **79**,1413 (1983).
12. Iftikhar A.Awan and Tahira Mahmood, *J. Chem. Soc. Pak.*, **1**(2), 87 (1999).
13. P.D.Lark, B.R. Craven and R.C.L. Bosworth, *The Handling of Chemical Data*, Pergmon Press, Oxford, 138 (1968).
14. M. Trautz and K.Winkler, *J. Prakt.Chem.*, **104**, 53 (1922).
15. Iftikhar A. Awan and M. C. Flowers, *J. Chem. Soc., Faraday Trans 1*, **81**, 1415 (1985).