Kinetics of the Thermal Gas Phase Decomposition of Methylcyclopropanecarboxylate Using Static Method

I. A. AWAN*, M. ALI, J. NISAR AND T. MAHMOOD
National Center of Excellence in Physical Chemistry
University of Peshawar, Peshawar

(Received 25th January, 2003, revised 8th February, 2005)

Summary: Thermal decomposition of methylcyclopropane-carboxylate (MCPC) was studied over the temperature range 682-793K and pressure between 5-50 Torr using static system. Isomerization reactions to give methyl-3-butenoate, methyl-2-butenoate (cis+trans) and methyl-2-propenoate accounted for 95% of the methycyclopropane-carboxylate decomposition.

These isomerizations are homogeneous first order, non-radical processes. The high pressure Arrhenius parameters are given in the rate equations:

$k_{total}/s^{-1}=10^{13.7\pm1.2}$ exp(-236.9±16.8kJ mol^{-1}/RT); $k_1/s^{-1}=10^{13.3\pm1.6}$ exp(-243.6±22.5kJ $mole^{-1}$/RT); $k_2/s^{-1}=10^{13.3\pm1.4}$ exp(-233.8±18.6 kJ$mole^{-1}$/RT); $k_3/s\text{-}1=10^{13.9\pm0.8}$ exp(-251.3±10.7 kJ$mole^{-1}$/RT)

Error limits quoted are statistically 95% certainty limits. The observed Arrhenius parameters are consistent with the biradical mechanism. Results from the present study are compared with those for cyclopropane isomerization to propene and it is found that the presence of CH3OC=O group on cyclopropane increases the rate constant for structural isomerization by lowering the activation energy for the reaction by 35 kJ $mole^{-1}$.

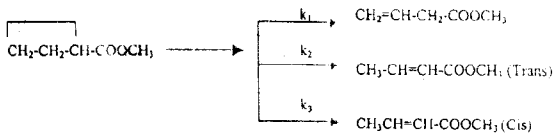
Introduction

The kinetics of the thermal gas phase decomposition of substituted cyclopropane has been of interest to kineticists due to their frequent use as a model. The kinetics results from these studies supported biradical mechanism in which a biradical is formed with C-C bond rupture followed by vicinal hydrogen transfer [1-2]. Thermal studies of alkyl [3], vinyl [4], phenyl [5], cyno [6] and methoxy [7] substituted cyclopropane all have been explained in terms of biradical mechanism. The observed Arrhenius parameters for these studies are consistent with the stabilization effects, which these substituents give to the radical centers. Gajewski et al [8] while studying the pyrolysis of alkyl -2-methyl - and 2,3-dimethylcyclopropane carboxylate observed that substitution of a carbonyl group on cyclopropane reduces the thermal geometric to structural isomerization rate ratio from 20-50 to 5-14.

No study on the thermal stability of methylcyclopropane carboxylate has been reported to date in the literature. Also, it is always of interest to expand database of relevant reactions. The work reported in this article was aimed to investigate the kinetics of the gas phase decomposition of methylcyclopropane carboxylate and to see if the structural isomerization products analogous to those observed for methyl and methoxy cyclopropanes are formed and, if so, to measure the effect of carbonyl group on the Arrhenius parameters for the structural isomerization of cyclopropane.

Results and Discussion

Kinetics of the thermal gas phase decomposition of methylcyclopropane carboxylate was studied in the temperature range 682-793 K. Initial runs were carried out in an aged unpacked reaction vessel. Methyl-3-butenoate and methyl-2-butenoate (*cis* and *trans*) were identified as structural isomerization products. The loss of the reactant accounts for the sum of the area of the isomerization products. Following reaction scheme summarizes the reaction pertinent to this study.



First order rate plots for the loss of the initial reactant (30 Torr initial reactant pressure) were linear

*To whom all correspondence should be addressed.

as shown in Fig 1. The overall first order decomposition rate constant (k_{total}) was calculated from the initial slope of this plot. As the overall rate is essentially first order, the plots of % product against % (total reaction) will be linear if the rate of formation is also first order, and therefore the slope of %(product) against %(total reaction) = k_i/k_{total} where k_i is the rate constant for the formation of individual product and k_{total} is the rate constant for the overall loss of reactant. Individual product plots at 692 K are shown in Figure 2. The individual rate constants for the products were measured using the initial slopes of the plots of percentage of the relevant reaction product against percentage overall reaction. The rate constants so determined are listed in Table-1. The following Arrhenius parameters were obtained from these rate constants:

$k_{total}/s^{-1}=10^{13.7\pm1.2}$ exp(-236.9±16.8kJ mol^{-1}/RT)

$k_1/s^{-1}=10^{13.3\pm1.6}$ exp(-243.6±22.5kJ $mole^{-1}$/RT)

$k_2/s^{-1}=10^{13.3\pm1.4}$ exp(-233.8±18.6 kJ$mole^{-1}$/RT)

$k_3/s^{-1}=10^{13.9\pm0.8}$ exp(-251.3±10.7 kJ$mole^{-1}$/RT)

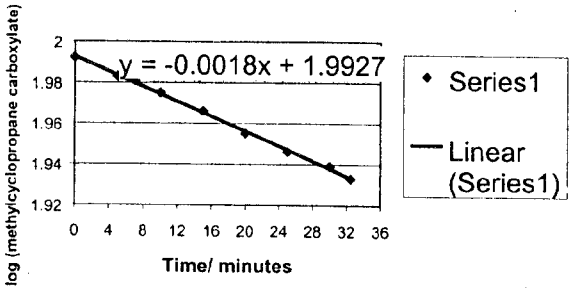


Fig. 1: First order rate plot for the loss of methylcyclopropanecarboxylate at 692 K (15 Torr initial pressure).

The error limits quoted are statistical 95 % certainty limits. The Arrhenius parameters were determined by a linear, non weighted least square procedure [9].

The pressure dependence on the reaction rates was investigated at 712 K. Total decomposition showed no change in rates within the experimental error, over the entire pressure range studied (5-50 Torr). Isomerization products rates were constant at high pressure but tended to fall off slightly at lower pressure.

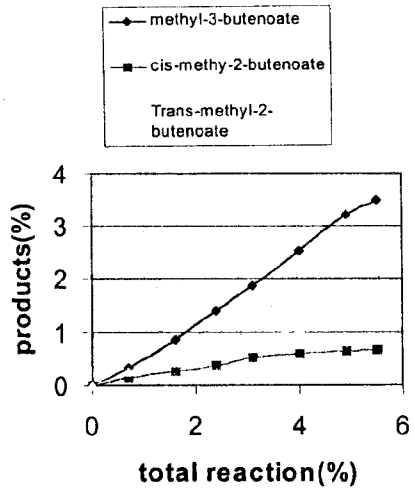
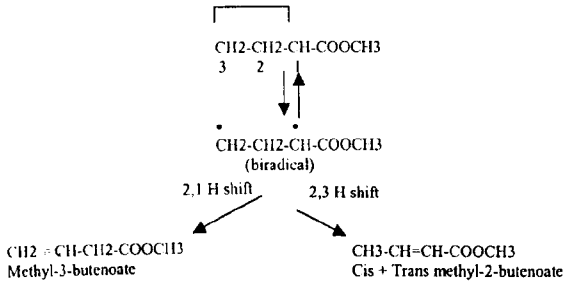


Fig. 2: Product distribution plot for methylcyclopropanecarboxylate pyrolysis at 692K (initial pressure 15 Torr).

The surface effect on the reaction was studied at 712 K using "aged" packed reaction vessel with 21 Torr initial reactant pressure. It was found that the overall reaction rate increased of an average of 14 %. The rates of production of isomerization products were constant.

The results of present study indicate that the initial decomposition of methylcyclopropane carboxylate yield isomeric products by first order reaction. The mode of decomposition seems to be in accord with that observed for other monosubstituted cyclopropanes. The absence of suitable type of alkyl group precludes olefin formation from the alkoxy portion of the molecule but the formation of structural isomeric products occurs as a result of ring cleavage at C1-C2 or C1-C3 followed by the vicinal H transfer to radical center.



The kinetics of pyrolysis of methylcyclopropanecarboxylate may be compared with those of other cyclopropane derivatives. From the data in

Table1. Rate constants for the decomposition of methylcyclopropane carboxylate with an initial pressure of 15 Torr in unpacked vessel.

Temp./K	$k_{(total)}$ 10^{-5} s^{-1}	$k_1/10^{-5}$ s^{-1}	$k_2/10^{-5}$ s^{-1}	$k_3/10^{-5}$ s^{-1}
682	4.46	2.50	0.47	0.41
692	6.91	3.85	0.81	0.94
702	9.87	7.02	1.19	1.38
718	29.00	16.10	3.21	3.30
722	42.20	21.80	5.87	5.05
728	60.80	35.10	7.40	7.75

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 ($NaNO_3$/ $NaNO_2$/KNO_3 ternary eutectic) thermostat. The temperature was maintained to ± 0.1°C by ADP 5 temperature controller. Temperature was measured with PT 100 resistance thermometer. Dead space of

Table 2. Rate constant at 665K for the gas phase thermal decomposition of some substituted cyclopropanes.

Reactant	k(total)/ $10^{-5}s^{-1}$	Log A/s^{-1}	E_a KJ $mole^{-1}$	Ref
Cyclopropane	0.8	15.5	272.0	11
Methylcyclopropane	1.2	14.8	260.7	3
Vinylcyclopropane	1595	13.5	207.5	4(a)
Phenylcyclopropane	5236	13.6	202.2	5
Methoxycyclopropane	41	14.02	243.0	7
Methylcyclopropane carboxylate	15.6	13.8	236.9	This work

Table-2 it is evident that substitution of -$COOCH_3$ on the cyclopropane increased the rate of decomposition. The lowering of the activation energy E_a by 35 KJ $mole^{-1}$ for methylcyclopropane-carboxylate in comparison to cyclopropane suggests that a biradical is involved in the ring cleavage process. The biradical formed from the methylcyclo-propanecarboxylate is expected to possess resonance energy comparable to a biradical formed from an alkylcyclopropane. From the data it is obvious that the presence of carbomethoxy substituent on the cyclopropane ring reduces the activation energy for the structural isomerization as well as lowers the 'A' factor; presumably in stabilizing the transition state and hence hinders the rotation of the carbomethoxy group. The 'A' factor and activation energy for these products are much closer to those observed for Alkyl vinyl cyclopropanes and thus in this case, in the transition state for H-atom transfer, the stablization due to carbomethoxy group is lost. Other studies of the carboalkyl cyclopropanes support the biradical mechanism and the magnitude of the effect of cabomethoxy substituent discussed above is consistent with those studies.

Experimental

Thermal kinetic studies were carried out as previously described [10] 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 length of pyrex tubing to give surface to volume ratio (S/V) of ca. 12 cm^{-1}, the other was of similar dimensions but was not

the reaction was 0.5 % and was ignored in calculations.

Analysis were carried out on a Shimadzu GC 7AG gas chromatograph using 30m x 0.25 mm Squalane WCOT maintained at ca. 0 °C 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 carboxylate was purchased from Aldrich company (USA) was 98 % pure and used without further purification.

Acknowledgement

Mukhtiar Ali wish to thank Education Department,Govt. of N.W.F.P.for the fellowship.

References

1. P. J. Robinson and K.A.Halbrook, Unimolecular Reactions, Wiley, London (1972).
2. W. Frost, Theory of Unimolecular Reactions, Academic Press, New York, (1973).
3. a) M. C. Flowers and H. M. Frey, *J.Chem.Soc.*, **39**, 53 (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).

4. a) M. C. Flowers and H. M. Frey, *J.Chem.Soc.*, 3547 (1961).
   b) C.A. Wellington, *J.Phy.Chem.*, **66**, 1671 (1962)
5. 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).
6. J. E. Baldin and C.G. Carter, *J.Am.Chem.Soc.*, **100,** 3942 (1978): **101**, 1325 (1979).
7. Iftikhar A. Awan and M.C. Flowers, *J.Chem.Soc., Faraday Trans. 1*, **79**,1413 (1983).
8. J.J. Gajewski and R.J. Weber, *J.Am.Chem.Soc.*, **99**, 816, (1977).
9. P.D.Lark, B.R. Craven and R.C.L. Bosworth, The Handling of Chemical Data, Pergmon Press, Oxford, 138 (1968).
10. Iftikhar A.Awan and Tahira Mahmood, *J. Chem. Soc. Pak.*, **21**(2), 87, (1999).
11. M. Trautz and K.Winkler, *J. Prakt.Chem.*, **104**, 53 (1922).