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# Kinetics of the Thermal Isomerization of Methylcyclopropane[†]

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Kinetic parameters for the unimolecular thermal isomerizations of methylcyclopropane to four isomeric butenes have been determined from rate constant measurements over a wide range of temperatures, 695−1154 K, using a single-pulse shock tube and a static reactor. For the overall reaction, $E_a = 64.4 \pm 0.3$ and $\log(A, s^{-1}) = 15.37 \pm 0.07$, values consistent with earlier studies at lower temperatures. The measured rate constants for the isomerization to *cis*- and *trans*-2-butene give $E_a = 63.3 \pm 0.3$ and $64.9 \pm 0.3$ kcal/mol, and $\log(A, s^{-1}) = 14.60 \pm 0.07$ and $14.75 \pm 0.06$, respectively, values in good agreement with the thermochemically based predictions of O'Neal and Benson. The similarity of kinetic parameters for the two reactions is consistent with the formation of the two 2-butenes through a common diradical intermediate. Kinetic data for 1-butene and 2-methylpropene formation are well represented by $E_a = 64.5 \pm 0.5$ and $66.4 \pm 0.2$ kcal/mol and $\log(A, s^{-1}) = 15.02 \pm 0.11$ and $14.81 \pm 0.05$. The higher $E_a$ for 2-methylpropene formation compared with $E_a$ for the production of 1-butene, and of *cis*- and *trans*-2-butene, is due to the higher energy required to break the C(2)−C(3) bond compared with the methyl-substituted C(1)−C(2) bond.

## Introduction

Kinetics of the thermal isomerizations of methylcyclopropane at relatively low temperatures attainable in a static reactor have been studied by a number of workers.[1,2] Chesick[1b] investigated the reaction at 713−763 K over a wide range of pressures. In the high-pressure range, the overall reaction was shown to be homogeneous with methylcyclopropane isomerizing to 1-butene, *cis*-2-butene, *trans*-2-butene, and 2-methylpropene in parallel first-order reactions. There was little cis−trans isomerization of 2-butenes. $E_a$ and log $A$ values deduced for the overall reaction were 65.0 kcal/mol and 15.45, respectively. In studies of the geometric and structural isomerization of methylcyclopropane and 1,2-dideuterio-3-methylcyclopropane carried out by Setser and Rabinovitch[2] at 653−693 K, the corresponding values for these parameters were 62.4 ± 0.6 kcal/mol and 14.61 ± 0.19, respectively. Assuming that this isomerization proceeds via a diradical intermediate, and using thermodynamic estimates of the transition state, O'Neal and Benson[3] predicted an activation energy of 64.2 kcal/mol. The difference in the two experimental $E_a$ values from each other, and from the predicted value, could be due to the small temperature ranges of these studies.

In the present study, a shock-tube and a static reactor have been used to investigate the isomerization of methylcyclopropane over a much larger temperature range, 695−1154 K, for the accurate determination of these parameters. An even more significant aspect of this investigation was to determine reliable values of the Arrhenius parameters for the conversion of methylcyclopropane to *cis*- and *trans*-2-butenes. While Chesick[1b] had reported only the activation parameters for the overall reaction, from his published rate constants Placzek and Rabinovitch[1a] calculated an activation energy of 68.1 kcal/mol for the formation of trans isomer, a value higher than that for the cis isomer by 4.2 kcal/mol. Work at 653−693 K by Setser and Rabinovitch[2] gave activation energies of 61.9 and 64.4 kcal/mol for the formation of the *cis*- and *trans*-2-butene, respectively. From their thermochemical calculations, O'Neal and Benson[3] predicted values of 63.0 kcal/mol for production of both isomers. By extending the temperature range by about 400 °C over that of the earlier work, we have tried to reconcile the differences between the experimental and the predicted values for the Arrhenius parameters.

## Experimental Section

**Materials.** Methylcyclopropane (99.95%) was obtained from API Standard Reference Materials. Matheson CP grade cyclopropane was added to reactant mixtures as an internal thermometer. 1-Butene (99.0%), *cis*-2-butene (95%), *trans*-2-butene (95%), and 2-methylpropene (99%), all Matheson CP grade obtained in lecture bottles, were used to prepare calibration samples for the products. The reagents were degassed through multiple freeze−pump−thaw cycles before use. Linde helium was used as the driver gas in the shock-tube runs.

**Sample Preparation.** For the shock tube runs methylcyclopropane was mixed with cyclopropane in different proportions and diluted with Matheson Research grade (99.9999%) argon. The mixtures were prepared, in 1 or 2 L glass storage flasks with greaseless stopcocks, from degassed samples of reagents and allowed to equilibrate before use for at least 3 days. The addition of cyclopropane was necessitated for the determination of the temperature attained during a shock run (see below).

For the shock-tube runs the methylcyclopropane/cyclopropane mixture compositions were 1.0%/1.0%, 2.0%/1.0%, and 1.3%/4.3% respectively. Mixtures for the static reactor runs had compositions of 2.0%/1.0% and 1.3%/4.3% respectively.

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**Apparatus.** The high-temperature experiments in this study were run in a 2.54 cm diameter single-pulse shock tube; the static reactor used for the lower temperature runs consisted of a 100 $cm^3$ glass cell surrounded by an aluminum furnace. Descriptions and operating procedures for these devices have been reported earlier.[4,5] Analyses of reactant and product samples were carried out on a Varian Model 1440-20 isothermal gas chromatograph with FID, using a 1.5 m 5% *n*-octane on Porasil C column at 43 °C in tandem with a 3 m column of polypropylene glycol saturated with $AgNO_3$ on 80−100 mesh Chromosorb W at room temperature. The polypropylene glycol column was also used alone for the separation of cyclopropane from propene, needed for the determination of the reaction temperature.

**Kinetic Runs.** For the shock-tube runs, 45−75 Torr samples of the methylcyclopropane−cyclopropane mixtures in argon were placed in the driven section of the tube, and the samples were heated for 800 ± 50 $\mu$s. The temperatures achieved in these runs ranged from 990 to 1154 K, as determined from the extent of conversion of cyclopropane to propene. At the end of the reaction the product samples were collected in 25 mL glass bulbs and analyzed chromatographically.

For the runs in the static reactor, 343 and 212 Torr sample mixtures were heated at 695−698 K. The heating times for these runs were 75 and 85 min, respectively. The temperatures were measured both directly using an Omega Engineering Model 650-J-D digital thermometer, and calculated from the extent of conversion of cyclopropane to propene. Two samples of the reaction products were collected simultaneously and chromatographed.

**Calculations.** Extents of conversion of methylcyclopropane to each of the four products, and of cyclopropane to propene, were determined from the GC peak heights, corrected for measured sensitivity differences of the various hydrocarbons. Rate constants were calculated assuming that both methylcyclopropane and cyclopropane underwent homogeneous first-order irreversible reactions.

The reaction temperatures were determined from the calculated rate constants for the cyclopropane isomerization to propene and the well-established Arrhenius parameters for this reaction: $E_a = 65.0$ kcal/mol and $\log(A, s^{-1}) = 15.2$.[6]

For each experiment, the rate constant for total consumption of methylcyclopropane was apportioned to rate constants for isomerization to 1-butene, *cis*-2-butene, *trans*-2-butene, and 2-methylpropene by multiplying the overall rate constant by the fraction of the corresponding component in the product mixture, following the evidence that these isomerizations are parallel, first-order reactions.[1b]

## Results and Discussion

**Product Distribution.** In both the shock-tube and the static-reactor runs, all four isomeric butenes (1-butene, *cis*-2-butene, *trans*-2-butene, and 2-methylpropene) were detected as major products, with 1-butene most abundant (over 40%) and 2-methylpropene least abundant (about 11%) in the majority of the runs. At static reactor temperatures the distribution of the products is quite consistent with those reported by Chesick[1b] and by Setser and Rabinovitch.[2] For example, their relative rate constants at 740 K for 1-butene:*cis*-2-butene:*trans*-2-butene:2-methylpropene were 1.00:0.63:0.28:0.16[1b] and 1.00:0.71:0.30:0.18,[2] respectively, while in the present study the relative amounts of these products at 698 K were found to be approximately 1.0:0.8:0.4:0.2.

At the higher temperatures obtained in the shock tube, however, the fractions of 2-methylpropene and *trans*-2-butene increased. The product ratios at the highest temperature were 1.00:0.60:0.54:0.28. Whereas the *cis*-2-butene to *trans*-2-butene ratio was 2.0 or higher at the lower temperatures in both the previous studies[1b,2] and the present investigation, at 1154 K the amount of *trans*-2-butene produced approached that of *cis*-2-butene, the cis to trans ratio becoming 1.1.

**Arrhenius Parameters.** Figure 1 shows the Arrhenius plots for the overall reaction methylcyclopropane → products, and for isomerization to the individual butenes from 18 shock-tube experiments and two static reactor runs. Linear least-squares fits for the data gave the following activation parameters:

for methylcyclopropane → all products:

$$\log(A, s^{-1}) = 15.37 \pm 0.07 \qquad E_a = 64.4 \pm 0.3 \text{ kcal/mol}$$

for methylcyclopropane → 1-butene:

$$\log(A, s^{-1}) = 15.02 \pm 0.11 \qquad E_a = 64.5 \pm 0.5 \text{ kcal/mol}$$

for methylcyclopropane → *cis*-2-butene:

$$\log(A, s^{-1}) = 14.60 \pm 0.07 \qquad E_a = 63.3 \pm 0.3 \text{ kcal/mol}$$

for methylcyclopropane → *trans*-2-butene:

$$\log(A, s^{-1}) = 14.75 \pm 0.06 \qquad E_a = 64.9 \pm 0.3 \text{ kcal/mol}$$

for methylcyclopropane → 2-methylpropene:

$$\log(A, s^{-1}) = 14.81 \pm 0.05 \qquad E_a = 66.4 \pm 0.2 \text{ kcal/mol}$$

The activation energy of 64.4 kcal/mol and the log *A* value of 15.37 for the overall reaction agree well with values of 65.0 kcal/mol and 15.45 determined by Placzek and Rabinovitch[1a] from Chesick's data at 713−763 K;[1b] these values are somewhat higher than those reported by Setser and Rabinovitch,[2] 62.4 kcal/mol and 14.61, from their work at 693−748 K.

Assuming that most three-membered ring compounds undergo isomerization via the formation of a diradical intermediate, Benson and O'Neal have made a priori estimates of the Arrhenius parameters for these reactions.[3] Our experimental values are in excellent agreement with their estimates of 64.2 kcal/mol for $E_a$ and 15.2 for log *A* for methylcyclopropane isomerization to all products. The activation energy of 65.0 kcal/mol for the cyclopropane to propene isomerization via a diradical is now well established.[6] Substitution of a methyl group for an H atom on one of the cyclopropane carbons is expected to lower the strength of the adjacent carbon−carbon bond[7] and should lead to an activation energy slightly lower than 65.0 kcal/mol. The present work extending the earlier low-temperature study upward to 1154 K shows that the Arrhenius parameters for the overall reaction are essentially constant over a wide range of temperature.

The activation energy for the isomerization of methylcyclopropane to *trans*-2-butene in the present study appears to be higher by 1.6 ± 0.4 kcal/mol than $E_a$ for the conversion to *cis*-2-butene. This difference is significantly smaller than the 4.2 kcal/mol, calculated from Chesick's data,[1b] and smaller but comparable to 2.5 ± 0.8 kcal/mol obtained by Setser and Rabinovitch,[2] in studies done over narrow temperature ranges of 50 and 40 K. From their thermochemical calculations, O'Neal and Benson[3] predicted an activation energy of 63.0 kcal/mol

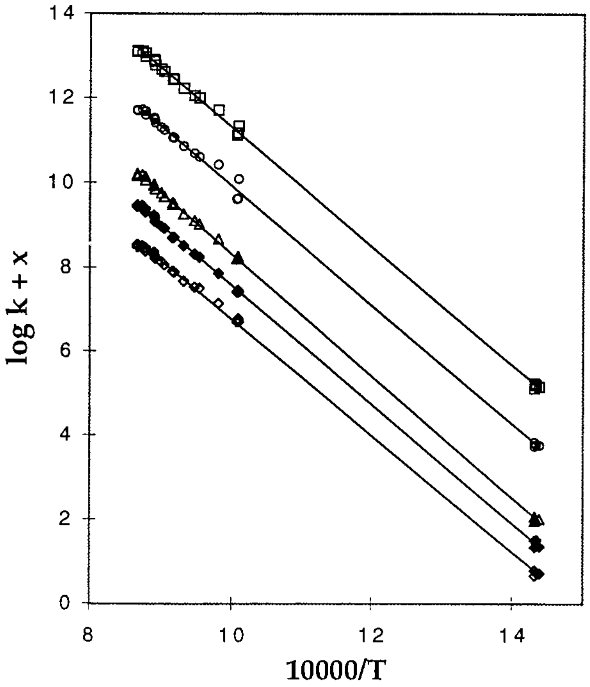

**Figure 1.** Rate constants *k* for the isomerization of methylcyclopropane to various butenes: (□) all products ($x = 10$); (○) 1-butene ($x = 9$); (△) 2-methylpropene ($x = 8$); (◆) *trans*-2-butene ($x = 7$); (◇) *cis*-2-butene ($x = 6$).

for formation of both these isomers. If these 2-butenes come from the same diradical intermediate produced by breaking the C(1)−C(2) bond, but form products via different rotational exit channels, a slight difference in the apparent activation energies would be expected if the proportion exiting via each channel is temperature dependent.

That the reaction channel involved in the formation of 1-butene is different from the one leading to the 2-butene isomers is indicated by the fact that over almost the entire temperature range, the ratio of the 1-butene concentration to the sum of the 2-butenes in the product mixture is about 0.9 and not 1.0. A least-squares fit of the data for total 2-butene formation leads to values of $E_a = 63.9$ kcal/mol and $\log(A, s^{-1}) = 14.95$, values consistent with the Benson and O'Neal predictions.

The activation energy of 66.4 ± 0.2 kcal/mol for the formation of 2-methylpropene via the diradical formed by breaking the C(2)−C(3) bond is in excellent agreement with the values calculated from Chesick's data and from O'Neal and Benson's calculations, 66.0 and 65.8 kcal/mol, respectively. This results from breaking the C−C bond $\beta$ to the methyl substitution, in contrast to the other three products which come from an $\alpha$ cleavage.

## Conclusions

The Arrhenius parameters for the thermal isomerization of methylcyclopropane to different butenes have been redetermined over a wide range of temperatures. The activation energies and the preexponential factors for the overall reaction, and for the isomerization to 2-methylpropene are consistent with the earlier values determined by Chesick[1b] and predicted from the thermochemical calculations of O'Neal and Benson.[3] This work has shown that the these values are reliable even at much higher temperatures than previously explored.

The difference in activation energies, $\Delta E_a$, for the isomerization to *cis*- and to *trans*-2-butene is revised downward to 1.6 ± 0.4 kcal/mol, as determined from the present data covering temperatures from 696 to 1154 K. This value is much smaller than the 4.2 kcal/mol calculated from Chesick's data. The source of this former large value was the seemingly high $E_a$ of 68.1 kcal/mol for the methylcyclopropane → *trans*-2-butene isomerization. In comparison, $\Delta E_a$ determined by Setser and Rabinovitch is 2.5 kcal/mol. It is reasonable to assume that one diradical precursor leads to these two isomeric products by following two different exit channels.

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## References and Notes

(1) (a) Placzek, D. W.; Rabinovitch, B. S. *J. Phys. Chem.* **1965**, *69*, 2141−2145. (b) Chesick, J. P. *J. Am. Chem. Soc.* **1960**, *82*, 3277−3285.

(2) Setser, D. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1964**, *86*, 564−569.

(3) (a) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866−1887. (b) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas-Phase Unimolecular Reactions"; NSRDS NBS 21, U.S. Government Printing Office, Washington, DC, 1970; p 225.

(4) Lewis, D. K.; Giesler, S. E.; Brown, M. S. *Int. J. Chem. Kinet.* **1978**, *10*, 277−294.

(5) Lewis, D. K.; Bergman, J.; Manjoney, R.; Paddock, R.; Kalra, B. L. *J. Phys. Chem.* **1984**, *88*, 4112−4116.

(6) (a) Bradley, J. N.; Frend, M. A. *Trans. Faraday Soc.* **1971**, *67*, 72. (b) Jeffers, P. M.; Lewis, D. K.; Sarr, M. S. *J. Phys. Chem.* **1973**, *77*, 3037−3041.

(7) Rossi, A. R. *J. Phys. Chem.* **1979**, *83*, 2554−2556.