

Isomerization and Decomposition of 2,3-Dimethyloxirane. Studies with a Single-Pulse Shock Tube

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The isomerizations and decompositions of *cis*- and *trans*-2,3-dimethyloxirane were studied behind reflected shocks in a pressurized driver single-pulse shock tube over the temperature range 900–1150 K and overall densities of $\sim 3 \times 10^{-5}$ mol/cm³. In addition to a *cis* \rightleftharpoons *trans* structural isomerization, four isomerization products, methyl ethyl ketone, isobutyraldehyde, ethyl vinyl ether, and 2-butene-3-ol, were obtained under shock heating. A large number of decomposition products were also obtained. The major ones in decreasing order of abundance were CO, C₂H₄, C₂H₆, and CH₄. In a similar manner to the decomposition of oxirane and methyloxirane, the free-radical reactions in the present system are initiated by a direct decomposition of a thermally excited methyl ethyl ketone which is produced in the course of the isomerization. A reaction scheme composed of 41 species and 65 elementary reactions accounts for the product distribution over the entire temperature range of this investigation provided decomposition channels of thermally excited isomers are included in the scheme. The rate constants obtained for the isomerization reactions are in good agreement with the values extrapolated from low temperatures. First-order Arrhenius rate parameters for the formation of the various reaction products are given and a sensitivity analysis for their production is summarized.

I. Introduction

We have recently published a detailed investigation on the high-temperature isomerization and decomposition of methyl-oxirane (propylene oxide).¹ We have demonstrated by the use of isotope labeling that all the isomerization products were produced by unimolecular processes although two of them, methyl vinyl ether and allyl alcohol, required very complex transition structures. We have also verified, by computer simulation, the postulate that the initial production of free radicals comes from the dissociation of thermally excited isomers. The latter are produced with excess thermal energy during the isomerization processes.

2,3-Dimethyloxirane is another member of the epoxy family of molecules. It appears in the form of two isomers, *cis* and *trans*. When it is subjected to high temperatures, similar processes, which are initiated by opening of the unstable epoxy ring, take place. Flowers and Parker² performed a very thorough investigation of the thermal reactions of this molecule in the temperature range 668–740 K. They found four structural isomers: methyl ethyl ketone, isobutyraldehyde, ethyl vinyl ether, and 3-buten-2-ol. They determined Arrhenius parameters for the rates of their formation and discussed their kinetic mechanism. They also found that the *cis* \rightarrow *trans* isomerization had a much lower rate than the structural isomerizations. Several decomposition products were mentioned in the article but neither Arrhenius parameters nor a discussion on the mechanism of their production was given.

We are not aware of any study at higher temperatures where the decomposition reactions and the role of free-radical processes become more important. One of the purposes of this investigation is to measure the production rates of the individual decomposition and isomerization products and to elucidate their kinetic mechanisms. A detailed mechanism is thus suggested, a reaction scheme is constructed, and computer simulation of the isomerization and decomposition products is performed.

II. Experimental Section

1. Apparatus. The thermal reaction reactions of 2,3-dimethyloxirane were studied behind reflected shocks in a

pressurized driver, 52 mm i.d. single-pulse shock tube. The tube and its mode of operation have been described in an earlier publication³ and will be reviewed here only briefly.

The driven section was 4 m long and the driver had a variable length up to a maximum of 2.7 m. It could be varied in small steps in order to obtain the best cooling conditions. A 36-L dump tank was connected to the driven section at 45° angle near the diaphragm holder in order to prevent reflection of transmitted shocks. The driven section was separated from the driver by Mylar polyester film of various thickness depending upon the desired shock strength. Postshock samples were collected from the tube through an outlet in the driven section (near the end plate) and were analyzed on a Hewlett-Packard Model 5890A gas chromatograph.

Reflected shock temperatures were calculated from the extent of isomerization of cyclopropanecarbonitrile (cpcn) which was added in small quantities to the reaction mixture to serve as an internal standard. The temperatures were calculated from the relation

$$T = -(E/R)/\ln\left\{-\frac{1}{A_t}\ln(1 - \chi)\right\} \quad (\text{I})$$

where t is the reaction dwell time and χ is the extent of isomerization defined as

$$\chi = [\text{isomeric products}]_t / ([\text{isomeric products}]_t + [\text{cpcn}]_t) \quad (\text{II})$$

The isomerization is a first-order unimolecular reaction⁴ with a rate constant $k_{1st} = 10^{14.58} \exp(-57.8 \times 10^3/RT) \text{ s}^{-1}$.

Compression ratios behind the reflected shocks were calculated from the measured incident shock velocities using the three conservation equations and the ideal gas equation of state. The molar enthalpies of 2,3-dimethyloxirane for these calculations were taken from Stull *et al.*⁵ The velocities were measured with two miniature high-frequency pressure transducers (Vibrometer Model 6QP500) placed 300 mm apart near the end plate of the driven section. The signals generated by the shock wave passing over the transducers were fed through a home-built piezo amplifier to a Nicolet Model 3091 digital oscilloscope. Time intervals between the two signals shown on the

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TABLE 1: Experimental Conditions and Product Distribution in the Decomposition of *cis*-2,3-Epoxybutane^a

| <i>T</i> ₅ , K | <i>t</i> , ms | <i>C</i> ₅ × 10 ⁵ | <i>c</i> -EB | MEK | IBA | BOL | <i>t</i> -EB | EVE | CO | CH ₄ | C ₂ H ₄ | C ₂ H ₆ | C ₂ H ₂ | C ₃ H ₆ | C ₄ H ₆ | PO |
|---------------------------|---------------|---|--------------|-------|--------|-------|--------------|--------|--------|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--------|
| 900 | 2.06 | 2.05 | 99.97 | | | | 0.0201 | | | | 0.0067 | 0.0041 | | | | |
| 900 | 2.25 | 2.87 | 99.69 | 0.295 | | | | | | | 0.0129 | 0.0044 | | | | |
| 923 | 2.25 | 2.66 | 99.32 | 0.463 | | | 0.0878 | | 0.0300 | 0.0389 | 0.0417 | 0.0157 | | 0.0046 | | |
| 926 | 2.16 | 2.86 | 98.82 | 0.587 | | 0.363 | 0.133 | | 0.0268 | | 0.0474 | 0.0196 | | 0.0054 | | |
| 975 | 2.14 | 2.64 | 91.56 | 3.78 | | 0.772 | 1.66 | 0.234 | 0.152 | 0.214 | 0.439 | 0.172 | | 0.0642 | 0.0744 | 0.102 |
| 998 | 2.06 | 2.60 | 83.46 | 8.40 | | 1.32 | 3.00 | 0.518 | 0.0767 | 0.384 | 0.937 | 0.348 | 0.0051 | 0.155 | 0.136 | 0.279 |
| 1031 | 2.21 | 2.15 | 65.22 | 13.39 | 4.58 | 2.62 | 5.64 | 0.902 | 1.27 | 0.717 | 2.21 | 0.759 | 0.0141 | 0.426 | 0.354 | 0.888 |
| 1074 | 2.10 | 2.36 | 39.06 | 25.11 | 2.81 | 4.22 | 7.23 | 0.395 | 5.19 | 1.65 | 6.48 | 2.23 | 0.0986 | 1.52 | 0.951 | |
| 1117 | 2.14 | 3.65 | 9.34 | 32.99 | 13.12 | 4.87 | 5.27 | 0.0167 | 9.55 | 3.09 | 10.11 | 3.09 | 0.226 | 2.59 | 1.47 | 1.73 |
| 1128 | 2.14 | 1.90 | 6.66 | 20.71 | 5.74 | 2.47 | 1.13 | 0.0012 | 22.75 | 5.85 | 19.64 | 6.43 | 0.483 | 4.98 | 2.06 | 0.339 |
| 1137 | 2.11 | 3.19 | 3.47 | 20.08 | 2.91 | 1.17 | 0.503 | 0.0008 | 26.02 | 6.25 | 18.26 | 5.43 | 6.781 | 4.52 | 1.75 | 0.632 |
| 894 | 1.71 | 2.89 | 99.49 | 0.209 | 0.145 | | 0.154 | | | | 0.0051 | 0.0018 | | | | |
| 902 | 1.63 | 2.67 | 99.01 | 0.347 | 0.158 | | 0.397 | 0.0028 | | 0.0122 | 0.0128 | 0.0056 | | | | |
| 911 | 2.18 | 2.42 | 99.25 | 0.365 | 0.0843 | | 0.210 | 0.0025 | | 0.0173 | 0.0215 | 0.0105 | | 0.0031 | | |
| 914 | 1.84 | 2.65 | 99.22 | 0.294 | 0.121 | | 0.303 | | | 0.0183 | 0.0172 | 0.0184 | | 0.0113 | | |
| 920 | 2.02 | 2.56 | 98.85 | 0.574 | 0.115 | | 0.287 | 0.0062 | | 0.0275 | 0.0401 | 0.0188 | 0.0014 | | | |
| 924 | 1.78 | 2.45 | 98.36 | 0.678 | 0.192 | | 0.547 | 0.0130 | | 0.0272 | 0.0311 | 0.0136 | | | | |
| 958 | 1.83 | 2.38 | 94.84 | 2.20 | 0.372 | 0.424 | 1.15 | 0.0826 | | 0.115 | 0.188 | 0.0845 | | 0.0283 | 0.0651 | 0.0332 |
| 987 | 2.18 | 1.98 | 84.86 | 5.74 | 2.42 | 1.18 | 2.83 | 0.304 | | 0.329 | 0.841 | 0.348 | 0.0057 | 0.158 | 0.0827 | 0.145 |
| 987 | 2.07 | 2.36 | 87.03 | 5.16 | 1.74 | 1.03 | 2.55 | 0.263 | | 0.407 | 0.598 | 0.248 | 0.0031 | 0.102 | 0.103 | 0.126 |
| 998 | 2.08 | 2.08 | 84.05 | 6.13 | 2.47 | 1.21 | 2.98 | 0.356 | | 0.352 | 0.926 | 0.381 | 0.0075 | 0.181 | 0.102 | 0.191 |
| 1031 | 2.03 | 2.25 | 67.56 | 12.37 | 5.57 | 2.36 | 5.48 | 0.676 | | 0.748 | 2.21 | 0.808 | 0.0223 | 0.455 | 0.299 | 0.671 |
| 1033 | 1.96 | 2.27 | 71.47 | 9.78 | 5.94 | 1.92 | 4.67 | 0.604 | | 0.723 | 2.08 | 0.779 | 0.0209 | 0.429 | 0.286 | 0.625 |

^a *c*-EB = *cis*-2,3-epoxybutane; MEK = methyl ethyl ketone; IBA = isobutyraldehyde; BOL = 3-butene-2-ol; *t*-EB = *trans*-2,3-epoxybutane; EVE = ethyl vinyl ether; PO = propylene oxide.

TABLE 2: Experimental Conditions and Product Distribution in the Decomposition of *trans*-2,3-Epoxybutane

| <i>T</i> ₅ | <i>t</i> , ms | <i>C</i> ₅ × 10 ⁵ | <i>c</i> -EB | MEK | IBA | BOL | <i>t</i> -EB | EVE | CO | CH ₄ | C ₂ H ₄ | C ₂ H ₆ | C ₂ H ₂ | C ₃ H ₆ | C ₄ H ₆ | PO |
|-----------------------|---------------|---|--------------|-------|-------|--------|--------------|--------|--------|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--------|
| 926 | 2.00 | 2.69 | 97.29 | 0.378 | | 0.145 | 0.404 | | | 0.0232 | 0.0146 | 0.0081 | | 0.0016 | 0.0122 | |
| 941 | 2.00 | 2.77 | 98.25 | 0.719 | | 0.258 | 0.537 | 0.0140 | 0.0624 | 0.0374 | 0.0370 | 0.0215 | | 0.0047 | 0.0151 | 0.0185 |
| 950 | 2.00 | 2.74 | 97.51 | 1.05 | | 0.417 | 0.701 | 0.0218 | 0.0667 | 0.0513 | 0.0529 | 0.0288 | | 0.0065 | 0.0202 | 0.0329 |
| 952 | 2.00 | 2.61 | 97.40 | 1.07 | | 0.350 | 0.834 | 0.0436 | 0.0074 | 0.0558 | 0.0578 | 0.0312 | | 0.0061 | 0.0179 | 0.0674 |
| 960 | 2.00 | 4.81 | 96.77 | 1.34 | | 0.545 | 0.868 | 0.0489 | 0.0905 | 0.0729 | 0.0623 | 0.0289 | | 0.0061 | 0.0254 | 0.0846 |
| 1004 | 2.00 | 5.00 | 88.05 | 5.76 | 0.759 | 1.72 | 1.86 | 0.162 | 0.319 | 0.245 | 0.337 | 0.148 | 0.0023 | 0.0413 | 0.0669 | 0.476 |
| 1013 | 1.91 | 5.54 | 85.26 | 6.44 | 1.35 | 2.16 | 2.21 | 0.164 | 0.726 | 0.299 | 0.451 | 0.199 | 0.0037 | 0.0584 | 0.0949 | 0.532 |
| 1042 | 2.00 | 2.71 | 72.01 | 11.62 | 1.68 | 3.59 | 3.99 | 0.178 | 2.84 | 0.599 | 1.39 | 0.656 | 0.0142 | 0.237 | 0.254 | 0.845 |
| 1066 | 2.00 | 2.77 | 58.72 | 17.96 | 3.14 | 5.04 | 4.44 | 0.207 | 2.94 | 1.01 | 2.66 | 1.17 | 0.0433 | 0.508 | 0.483 | 1.42 |
| 930 | 2.26 | 2.58 | 98.99 | 0.144 | 0.144 | 0.506 | 0.144 | 0.0058 | | 0.0185 | 0.0156 | 0.0072 | | | | 0.0063 |
| 940 | 2.18 | 2.42 | 96.69 | 1.12 | | 0.852 | 0.819 | 0.0444 | 0.0951 | 0.0708 | 0.0804 | 0.0459 | | 0.0091 | 0.0112 | 0.0576 |
| 941 | 2.31 | 2.40 | 97.66 | 0.705 | 0.147 | 0.701 | 0.418 | 0.0363 | 0.0775 | 0.0460 | 0.0537 | 0.0277 | | 0.0052 | | 0.0477 |
| 946 | 2.15 | 2.60 | 98.67 | 0.307 | 0.056 | 0.507 | 0.056 | 0.0177 | 0.245 | 0.0416 | 0.0300 | 0.0161 | | 0.0031 | | 0.0252 |
| 971 | 2.20 | 2.63 | 94.61 | 1.89 | 0.700 | 1.08 | 0.700 | 0.0817 | 0.365 | 0.102 | 0.141 | 0.0771 | | 0.0162 | 0.0115 | 0.163 |
| 972 | 2.16 | 2.28 | 93.32 | 2.41 | | 1.46 | 1.80 | 0.0908 | 0.212 | 0.129 | 0.193 | 0.105 | | 0.0213 | 0.0069 | 0.184 |
| 979 | 2.20 | 2.35 | 93.29 | 1.97 | 0.493 | 1.19 | 0.859 | 0.0991 | 1.32 | 0.154 | 0.199 | 0.104 | | 0.0239 | 0.0224 | 0.218 |
| 1000 | 2.21 | 2.14 | 88.09 | 4.53 | 1.29 | 1.91 | 1.29 | 0.194 | 0.823 | 0.278 | 0.540 | 0.259 | 0.0033 | 0.0751 | 0.0793 | 0.546 |
| 1002 | 2.16 | 2.35 | 90.97 | 4.02 | 1.29 | 0.0535 | 1.29 | 0.172 | 0.512 | 0.254 | 0.482 | 0.253 | | 0.0650 | 0.0613 | 0.493 |
| 1012 | 2.14 | 2.27 | 82.47 | 6.38 | 1.83 | 2.51 | 1.59 | 0.226 | 2.54 | 0.359 | 0.722 | 0.342 | 0.0029 | 0.108 | 0.112 | 0.729 |
| 1017 | 2.09 | 2.22 | 82.67 | 7.01 | 1.67 | 2.63 | 2.04 | 0.230 | 0.911 | 0.419 | 0.866 | 0.412 | 0.0045 | 0.133 | 0.128 | 0.787 |
| 1036 | 2.14 | 2.18 | 73.93 | 8.18 | 1.99 | 2.99 | 2.66 | 0.225 | 6.05 | 0.598 | 1.29 | 0.618 | 0.0140 | 0.212 | 0.166 | 0.981 |
| 1044 | 2.10 | 2.23 | 69.86 | 12.16 | 4.19 | 4.14 | 1.84 | 0.258 | 1.97 | 0.727 | 1.91 | 0.889 | 0.0192 | 0.343 | 0.307 | 1.25 |
| 1087 | 2.04 | 2.25 | 50.14 | 20.65 | 4.54 | | 4.04 | 0.201 | 5.70 | 1.88 | 5.61 | 2.35 | 0.103 | 1.14 | 0.881 | 2.00 |
| 1093 | 2.18 | 2.25 | 44.08 | 20.86 | 7.53 | 5.68 | 2.41 | 0.178 | 4.71 | 1.91 | 5.56 | 2.26 | 0.0809 | 1.15 | 0.823 | 1.99 |
| 1096 | 2.08 | 2.25 | 38.13 | 24.68 | 4.28 | 6.35 | 4.24 | 0.172 | 4.42 | 2.29 | 6.85 | 2.72 | 0.112 | 1.44 | 1.05 | 2.06 |
| 1102 | 2.07 | 2.15 | 40.04 | 20.63 | 4.85 | 5.42 | 3.68 | 0.161 | 7.19 | 2.32 | 7.10 | 2.89 | 0.115 | 1.47 | 1.07 | 2.19 |
| 1118 | 2.17 | 2.22 | 17.61 | 30.29 | 3.57 | 6.13 | 3.82 | 0.119 | 11.88 | 3.55 | 11.19 | 4.17 | 0.286 | 2.55 | 1.59 | 2.35 |

^a *t*-EB = *trans*-2,3-epoxybutane; MEK = methyl ethyl ketone; IBA = isobutyraldehyde; BOL = 3-butene-2-ol; *c*-EB = *cis*-2,3-epoxybutane; EVE = ethyl vinyl ether; PO = propylene oxide.

oscilloscope were obtained digitally with an accuracy of 2 μs (out of about 450), corresponding to approximately 15 K. A third transducer (P.C.B. Model 113A26) placed in the center of the end plate provided measurements of the reaction dwell times (approximately 1.8 ms) with an accuracy of ~5%. Cooling rates were approximately 5 × 10⁵ K/s.

2. Materials and Analysis. Reaction mixtures containing 1% of *cis*-2,3-dimethyloxirane and 1% of the *trans* isomer diluted in argon were prepared manometrically and stored at high pressure in stainless steel cylinders. Both the cylinders and the line were pumped down to better than 10⁻⁵ Torr before the preparation of the mixtures. 2,3-Dimethoxyloxirane was obtained from Aldrich Chemical Co. The *cis* isomer was listed as 97% pure and the *trans* isomer as 96% pure. The only impurity of interest was ~0.25% *trans* in the *cis* isomer. The

argon used was Matheson ultra-high-purity grade, listed as 99.9995%, and the helium was Matheson pure grade listed as 99.999%. All the materials were used without further purification.

The gas chromatographic analyses of the postshock mixtures were performed on two Porapak N columns connected in parallel to flame ionization and nitrogen phosphor detectors. The analyses of all the products except for CO were done with a FID and of the internal standard and its isomers with a NPD. The initial temperature of the columns was 35 °C and was gradually elevated to 190 °C in an analysis which lasted close to 2 h. Since the Porapak N column could not separate *cis*-2,3-dimethoxyloxirane from isobutyraldehyde, which is an isomerization product of 2,3-dimethoxyloxirane, an additional analysis was run for each experiment on a Porapak Q column which

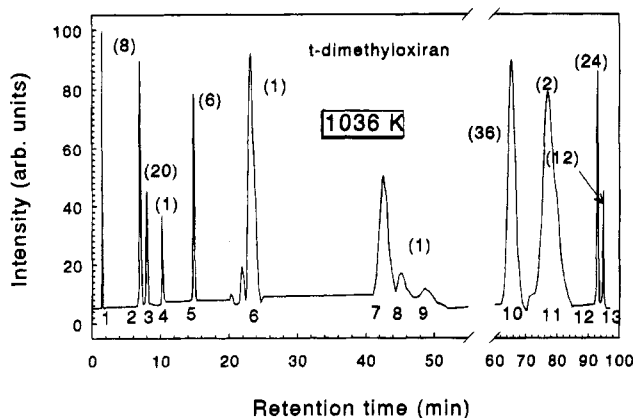


Figure 1. Gas chromatogram of a postshock mixture of 1% *trans*-2,3-dimethyloxirane in argon heated to 1036 K. The numbers by the chromatogram peaks indicate attenuation factors: (1) methane; (2) ethylene; (3) ethane; (4) acetylene; (5) propylene; (6) butadiene; (7) methyloxirane; (8) methyl vinyl ether; (9) propanal; (10) *trans*-2,3-dimethyloxirane; (11) *cis*-2,3-dimethyloxirane + isobutyraldehyde; (12) methyl ethyl ketone; (13) 3-buten-2-ol.

could separate these to compounds. From their ratio on the Porapak Q column and their sum on the Porapak N column, the concentration of each compound could be evaluated. A typical Porapak N chromatogram of a postshock mixture of 1% *trans*-2,3-dimethyloxirane in argon heated to 1036 K is shown in Figure 1.

Carbon monoxide was analyzed on a 2 m molecular sieve 5A column at 35 °C. It was reduced at 400 °C to methane prior to its detection using a Chrompak methanizer with a carrier composed of 50% hydrogen and 50% argon. From these analyses the ratio $[CO]/[C_2H_4]$ in each experiment was determined. These ratios together with the known ethylene concentration obtained in the Proapak N analyses, gave the concentration of CO for each run. The ratio $[CO]/[C_2H_4]$ in a standard mixture of ethylene and carbon monoxide was determined periodically for calibration.

The concentrations of the reaction products $C_5(pr)_i$ were calculated from their GC peak areas from the following relations:⁶

$$C_5(pr)_i = A(pr)_i / S(pr)_i \{ C_5(2,5\text{-dimethyloxirane})_0 / A(2,3\text{-dimethyloxirane})_0 \} \quad (\text{III})$$

$$C_5(2,3\text{-dimethyloxirane})_0 = \{ p_1 \times \% (2,3\text{-dimethyloxirane}) \times \rho_5 / \rho_1 \} / 100RT_1 \quad (\text{IV})$$

$$A(2,3\text{-dimethyloxirane})_0 = A(2,3\text{-dimethyloxirane})_t + \frac{1}{4} \sum N(pr)_i \times A(pr)_i / S(pr)_i \quad (\text{V})$$

In these relations $C_5(2,3\text{-dimethyloxirane})_0$ is the concentration of 2,3-dimethyloxirane behind the reflected shock prior to decomposition and $A(2,3\text{-dimethyloxirane})_0$ is the calculated GC peak area of 2,3-dimethyloxirane prior to decomposition (eq V) where $A(pr)_i$ is the peak area of a product i in the shocked sample, $S(pr)_i$ is its sensitivity relative to 2,3-dimethyloxirane, and $N(pr)_i$ is the number of its carbon atoms. ρ_5/ρ_1 is the compression ratio behind the reflected shock and T_1 is room temperature.

The identification of the reaction products was based on their GC retention times and was also assisted by Hewlett Packard Model 5970 mass-selective detector. The sensitivities of the various products to the FID and the NPD relative to 2,3-dimethyloxirane and cyclopropanecarbonitrile were determined from standard mixtures. The areas under the GC peaks were

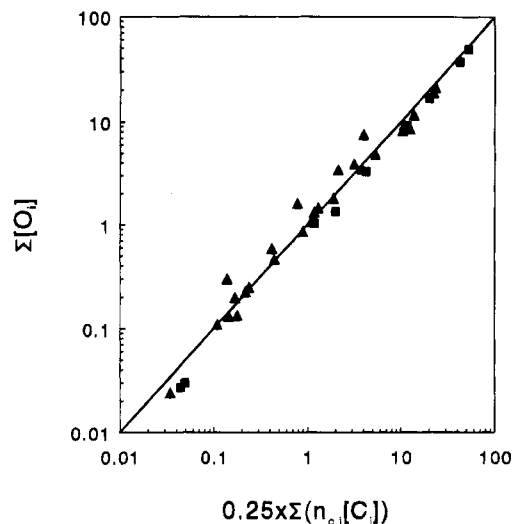


Figure 2. Oxygen-carbon mass balance among the decomposition products. Carbon monoxide is the oxygen-containing product of the highest concentration.

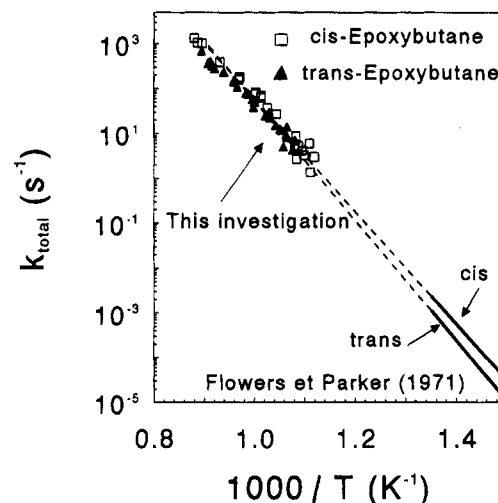


Figure 3. Arrhenius plot of the first-order rate constant for the overall reaction (isomerizations and decompositions) of 2,3-dimethyloxirane, integrated with a Spectra Physics Model SP4200 computing integrator and were transferred after each analysis to a PC for data reduction and graphical presentation.

III. Results

In order to determine the distribution of reaction products, tests were run with mixtures containing 1% *cis*-2,3-dimethyloxirane and *trans*-2,3-dimethyloxirane in argon, covering the temperature range 900–1150K. Details of the experimental conditions and the distribution of reaction products are given in Tables 1 and 2 for the *cis* and the *trans* isomers respectively. Methyl ethyl ketone is the isomer of the highest concentration, followed by isobutyraldehyde and 3-buten-2-ol. Among the decomposition products, carbon monoxide, ethylene, ethane, and methane are of the highest abundance.

The balance of oxygen vs carbon among the decomposition products is shown in Figure 2. The concentrations of carbon monoxide, propylene oxide, and propanal are plotted against one-fourth the sum of the concentrations of all the decomposition products (including the oxygen-containing species) each multiplied by the number of its carbon atoms. One-fourth is the ratio of oxygen to carbon in the reactant molecule. The 45° line in the figure represents a complete mass balance. As can be seen, within the limit of the experimental scatter, there is no major deviation from an oxygen-carbon balance over the temperature range of the investigation.

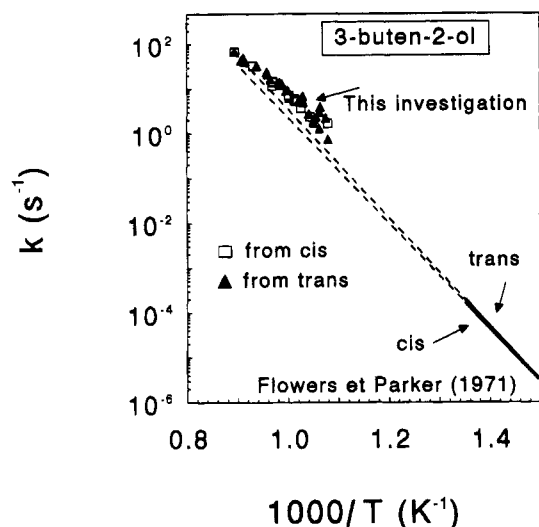


Figure 4. Arrhenius plot of the isomerization rate constant of the reaction 2,3-dimethyloxirane \rightarrow 3-buten-2-ol.

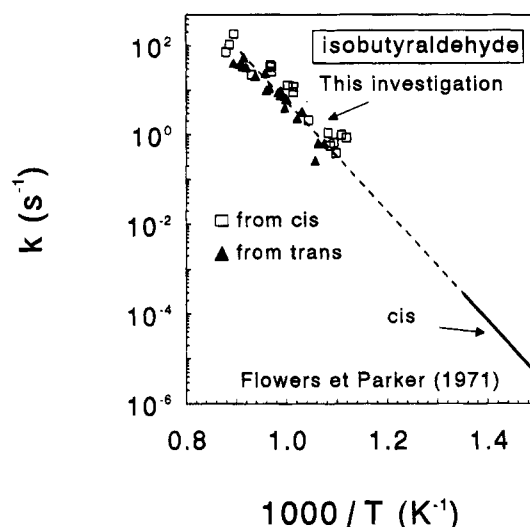


Figure 6. Arrhenius plot of the isomerization rate constant of the reaction 2,3-dimethyloxirane \rightarrow isobutyraldehyde.

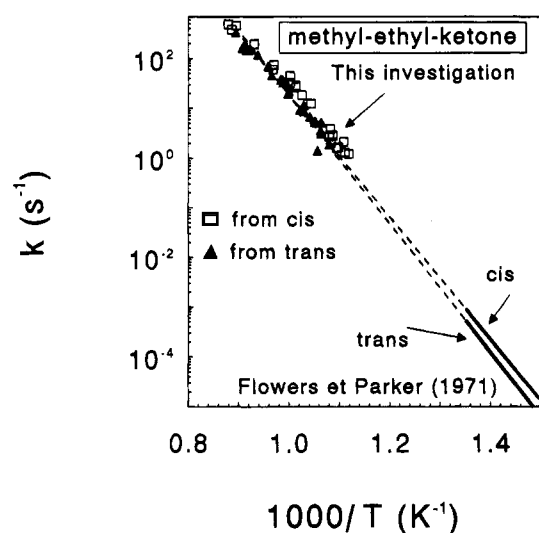


Figure 5. Arrhenius plot of the isomerization rate constant of the reaction 2,3-dimethyloxirane \rightarrow methyl ethyl ketone.

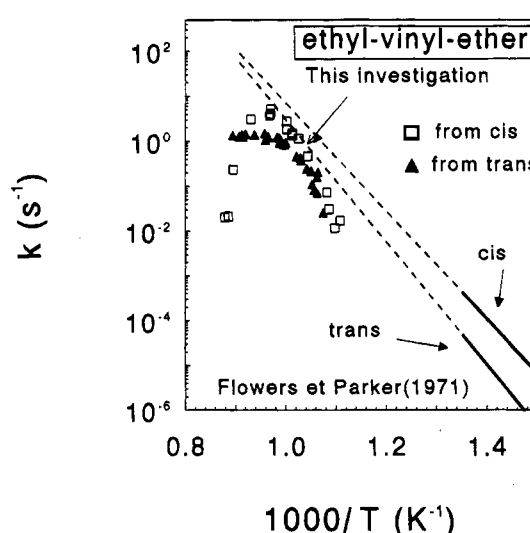


Figure 7. Arrhenius plot of the isomerization rate constant of the reaction 2,3-dimethyloxirane \rightarrow ethyl vinyl ether.

TABLE 3: First-Order Arrhenius Parameters for the Isomerization Products from the *cis* Isomer (900–1150 K)

| molecule | Flowers <i>et al.</i> ² | | this investigation | |
|---------------------|------------------------------------|-------------|------------------------|-------------|
| | log A, s ⁻¹ | E, kcal/mol | log A, s ⁻¹ | E, kcal/mol |
| methyl ethyl ketone | 13.60 | 56.32 | 13.78 | 56.32 |
| ethyl vinyl ether | 12.94 | 55.23 | 12.40 | 55.23 |
| isobutyraldehyde | 12.99 | 55.97 | 13.29 | 55.97 |
| 2-buten-3-ol | 12.18 | 53.99 | 12.58 | 53.99 |
| trans | 14.59 | 61.83 | — | — |

Figure 3 shows the rate constant for the overall reaction, isomerizations and decompositions, for each one of the two 2,3-dimethyloxirane isomers calculated as first-order rate constants using the relation:

$$k_{\text{total},\text{cis}} = -\ln\{[2,3\text{-dimethyloxirane}]_{\text{cis},t} / [2,3\text{-dimethyloxirane}]_{\text{cis},0}\} / t \quad (\text{VI})$$

The overall reaction rate constants obtained at low temperatures by Flowers and Parker² for the *cis* and for the *trans* isomers are also shown in the figure for comparison. The extrapolated lines which correspond to activation energies of 61.2 kcal/mol for the *trans* and 57.3 kcal/mol for the *cis* isomer fall inside the range of the data obtained in the present investigation with a much lower separation between the isomers, the *cis* being slightly more reactive. Altogether the rate constants obey an

Arrhenius temperature dependence of over 8 orders of magnitude variation (10^{-5} – 10^3). Figures 4–7 show Arrhenius plots of the first-order rate constants of the isomerization products methyl ethyl ketone, isobutyraldehyde, 3-buten-2-ol, and ethyl vinyl ether. They are calculated from the relation

$$k(\text{isomerization}) = [\text{isomer}]_t / \{ [2,3\text{-dimethyloxirane}]_0 - [2,3\text{-dimethyloxirane}]_t \} k_{\text{total}} \quad (\text{VII})$$

In all the figures the rate constants obtained at low temperatures by Flowers and Parker² are shown for comparison for both the *cis* and the *trans* isomers. The rate constants for the *cis* isomer are in all cases somewhat higher than those of the *trans* isomer both at high and at low temperatures. Table 3 summarizes the preexponential factors which were used in the reaction scheme for computer simulation in comparison with the values obtained at low temperatures, assuming the same activation energies. The rate of 3-buten-2-ol production is slightly higher than the one extrapolated from low temperatures and that of ethyl vinyl ether is lower. Both of these isomers decompose strongly at the high temperature end in the present study.

Figure 8 shows an Arrhenius plot of the rate constants for the *cis* \rightarrow *trans* and the *trans* \rightarrow *cis* isomerizations. As this channel is a minor one in the line of isomerizations and since the decomposition channels become very important at high

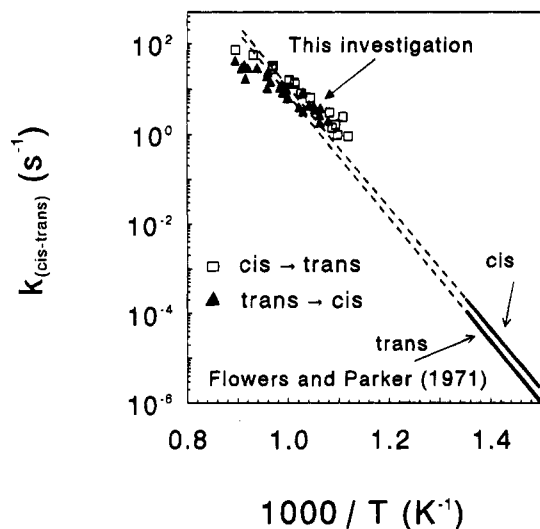


Figure 8. Arrhenius plot for the *cis* → *trans* isomerization of 2,3-dimethyloxirane.

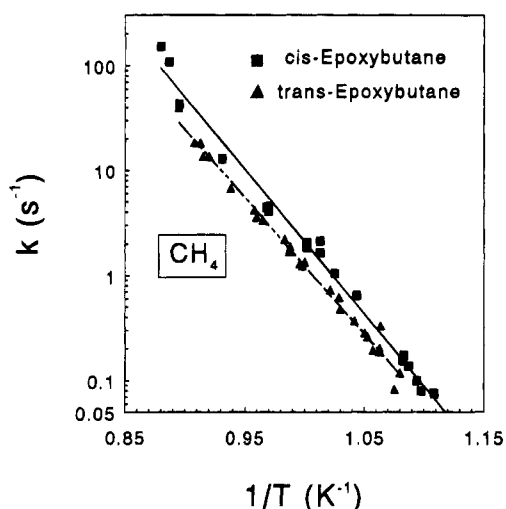


Figure 9. Arrhenius plot for the production of methane.

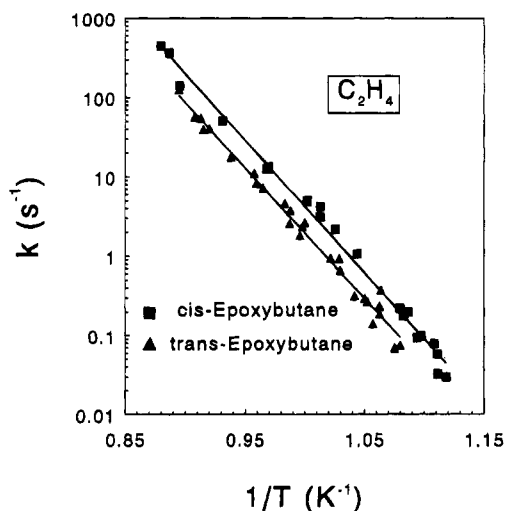


Figure 10. Arrhenius plot for the production of ethylene.

temperatures, it is almost impossible to determine Arrhenius parameters for the *cis* ⇌ *trans* isomerization. Since, however, the extrapolated low-temperature rate constants fall inside the range of the data obtained in the present investigation we believe that similar parameters prevail at the high temperatures.

Figures 9–11 show, as a few examples, Arrhenius plots of the first-order rate constants for production of methane, ethylene,

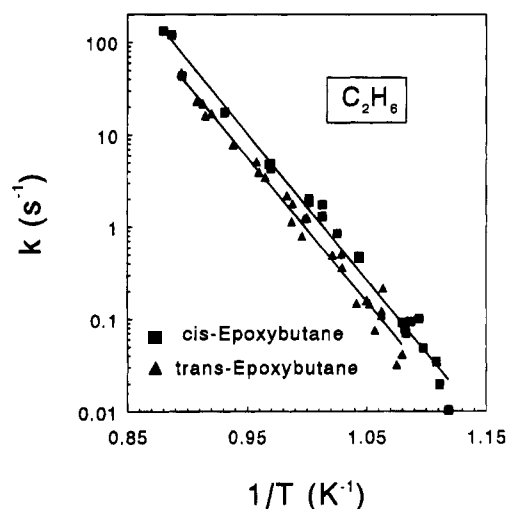


Figure 11. Arrhenius plot for the production of ethane.

TABLE 4: First-Order Arrhenius Parameters for Product Formation (900–1150 K)

| molecule | from <i>cis</i> | | from <i>trans</i> | |
|------------------------------|------------------------|-------------|------------------------|-------------|
| | log A, s ⁻¹ | E, kcal/mol | log A, s ⁻¹ | E, kcal/mol |
| methane | 14.07 | 62.9 | 13.05 | 59.3 |
| ethylene | 17.31 | 76.3 | 16.72 | 75.2 |
| ethane | 16.07 | 72.5 | 15.63 | 71.6 |
| acetylene | 18.30 | 90.5 | 19.37 | 97.5 |
| propylene | 17.46 | 80.3 | 17.61 | 83.1 |
| butadiene | 13.74 | 63.3 | 13.98 | 65.9 |
| propanal | 9.95 | 43.1 | 9.33 | 43.9 |
| propylene oxide ^a | 14.77 | 67.2 | | |
| carbon monoxide ^a | 16.48 | 72.7 | | |

^a No clear difference between the *cis* and the *trans* isomer.

and ethane. They were calculated from a relation similar to (VII), namely,

$$k_{\text{product}(i)} = [\text{product}]_{i,t} / \{ [\text{2,3-dimethyloxirane}]_0 - [\text{2,3-dimethyloxirane}]_t \} k_{\text{total}} \quad (\text{VIII})$$

As can be seen in all the three cases (and also in other products), the *cis* isomer is slightly more reactive than the *trans* isomer.

Values of *E* in units of kcal/mol for the decomposition products as obtained from the slopes of the lines and their corresponding preexponential factors are summarized in Table 4. It should be mentioned, however, that the parameters for the decomposition products do not represent elementary unimolecular reactions. They simply offer a useful way to present the experimental results and do not imply that the decomposition of 2,3-dimethyloxirane under the conditions of the present experiment is unimolecular.

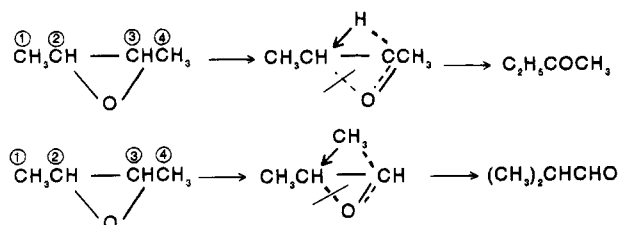
IV. Discussion

1. Isomerizations. In a recent study on the thermal reactions of methyloxirane (propylene oxide)¹ we have demonstrated, by isotope labeling, that all four isomerization products which were found in the system were obtained by direct unimolecular reactions of the reactant molecule. Two of the isomerization rate constants, those of methyl vinyl ether and allyl alcohol, had rather low preexponential factors which hinted at very stiff transition structures. Although there were enough free radicals in the system that, in principle, could recombine to produce these products (e.g., CH₃• + CH₂=CH-O• → CH₂=CH-O-CH₃), it was unequivocally proven that their formation was indeed unimolecular. We have not carried out an isotope distribution study in the present work but have a good reason

to assume, as has also been suggested in the low-temperature investigation,² that 2,3-dimethyloxirane behaves in a similar manner to that of methyloxirane, namely, all the structural and geometrical isomerizations occur as the result of nonradical unimolecular reactions.

Methyloxirane is an asymmetric molecule. 1,2 H-atom migration from position 2 to position 3 is not equivalent to an H-atom migration from position 3 to 2. One channel produces dimethyl ketone and the other channel produces propylaldehyde. 2,3-Dimethyloxirane, on the other hand, is symmetrical. 1,2 H-atom migration from position 2 to position 3, which produces methyl ethyl ketone, is identical to 1,2 H-atom migration from position 3 to 2. Both produce the same product. Production of isobutyraldehyde, which is the aldehyde formed in the present system, can proceed only by a 1,2 methyl group migration from position 2 to position 3 or vice versa, rather than 1,2 H-atom migration.

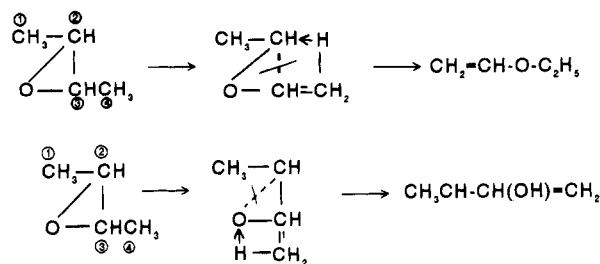
Both of these migrations can take place by cleavage of the C(2)-O (or C(3)-O) bond to form a biradical, followed by 1-4 hydrogen atom or methyl group migrations. Alternatively, they can proceed by concerted processes in which 1-2 migrations take place while the C(2)-O (or C(3)-O) bond, although highly extended, is still intact. In the low-temperature



study of Flowers *et al.*,² the structural isomerizations were assumed to proceed via biradical mechanism where cleavage of bonds occurs prior to migrations. This was assumed even though some of the preexponential factors obtained were below 10^{13} s^{-1} , a finding that does not support such a mechanism. The rate constants for the structural isomerizations which were obtained in this investigation fit quite well, with only small variations, the values extrapolated from the low-temperature studies. In view of the long extrapolation (several orders of magnitude in the rate constants), we can safely assume, as we did in the simulation studies, that the activation energies of these reactions are roughly the same at the low and the high temperatures. Thus, the preexponential factors which were obtained in this investigation are also too low to support a biradical mechanism (see Table 3).

As can be seen in Table 3, there is no difference in the activation energies, in the present system, between 1,2 H-atom (methyl ethyl ketone) and 1,2 methyl group (isobutyraldehyde) migrations. Both are around 56 kcal/mol. Normally, one would expect a higher activation energy for methyl group migration as has been observed, for example, in the isoxazole-5-methylisoxazole system.^{7,8} If the production of isobutyraldehyde is indeed a concerted process, ($A \sim 10^{13} \text{ s}^{-1}$), then the C-O bond in 2,3-dimethyloxirane is broken simultaneously with the methyl group migration. This migration makes the accepting carbon atom partially secondary, a fact that weakens the C-O bond. This compensates for the higher energy required to migrate a CH₃ group.

The production of 3-butene-3-ol and ethyl vinyl ether has also low preexponential factors that hint at a concerted process rather than a biradical one. The production of these two isomers requires a simultaneous 1,3 H atom migration and a C-C or a C-O bond rupture. The transition structures for these two processes seem to be stiffer than for the other two structural



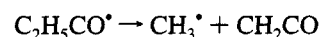
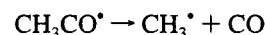
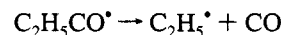
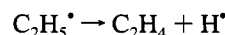
isomers owing to more severe simultaneous requirements. Indeed, according to the values obtained in this investigation, their preexponential factors (from the *cis* isomer) are the lowest, $10^{12.58}$ and $10^{12.40} \text{ s}^{-1}$, respectively.

A concerted process, however, cannot be attributed to the *cis* → *trans* isomerization. In order that this process will take place, the C(2)-O, C(3)-O, or C(2)-C(3) bonds must be completely broken to allow a free rotation. Indeed, the preexponentials ($10^{14.59}$ *cis*→*trans* and $10^{14.67}$ *trans*→*cis*) and the activation energies (61.8 and 63.0 kcal/mol) are the highest among the isomerization processes. Owing to the competition between 1,2 H-atom migration and free rotation-cyclization process, it is not inconceivable that some contribution to the structural isomerizations from this biradical mechanism does exist. But since the structure *cis* ⇌ *trans* isomerization does not constitute a major part of the overall isomerization, and since the free rotation-cyclization process has been shown in many systems to be much faster than H-atom migrations,⁹⁻¹⁴ this contribution must be very small.

2. Decompositions. It has already been shown, in the studies on the thermal reactions of oxirane¹⁵ and methyloxirane,¹ that in addition to the isomerizations considerable fragmentation takes place. This fragmentation yields, by consecutive reactions, a plethora of stable decomposition products.

The opening of the epoxy ring which results in the formation of more stable straight chain isomers is an exothermic reaction. In view of large differences in the heats of formation of the epoxy molecules and its isomers, the latter are produced with a large excess of thermal excitation. This excess energy is equal to $E_{\text{act}} + \Delta H_r$, where E_{act} is the activation energy of the C-O or C-C bond cleavage-rearrangement process and ΔH_r is the exothermicity of the isomerization reaction. The thermally excited products can either lose their energy by collision to produce the stable isomers or, alternatively, split up with the production of unstable intermediates that can initiate free radical reactions.

The energy diagram for these processes in 2,3-dimethyloxirane is shown in Figure 12. CH₃COC₂H₅ is formed with enough thermal energy which, if not lost by collisional deactivation, can decompose to CH₃CO* and C₂H₅* and also, although at a lower rate, to CH₃* and C₂H₅CO*. These free radicals further decompose according to



and begin a chain reaction which is carried by CH₃ radicals and H atoms.

All the other structural isomers are also produced with excess thermal energy but insufficient to allow decomposition to free radicals from the thermally excited states.

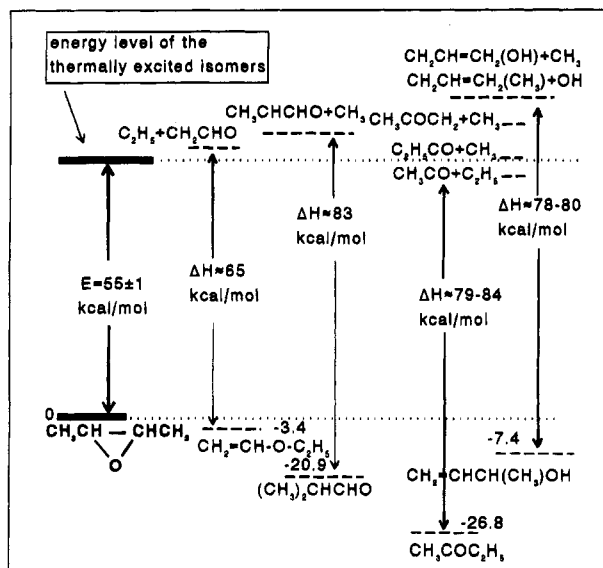


Figure 12. Energy diagram in the isomerization of 2,3-dimethyloxirane.

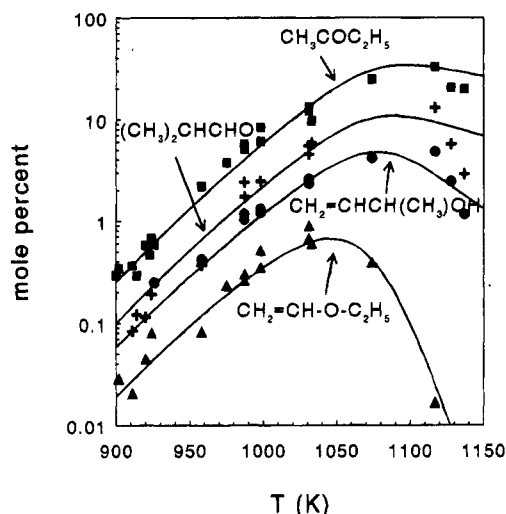


Figure 13. Experimental and calculated mole percent of the four isomerization products of 2,3-dimethyloxirane.

corresponding to the reactions as listed in the table. The rate constants are given as $k = AT^n \exp(-E/RT)$ in units of $\text{cm}^3/\text{mol} \cdot \text{s}$. Columns 4 and 5 give the values of the forward and reverse rate constants, at 1000 K, as calculated from the rate parameters and the equilibrium constants of the reactions at the same temperature. In column 6 the standard enthalpy change at 1000 K for each reaction is given. Column 7 shows the source of the rate parameters used.

The rate parameters assigned for the four unimolecular isomerizations (reactions 1–4) are based on the low-temperature data² with small changes in the preexponential factors in order to obtain the best fit to the experimental results.

The rate constants for the decomposition of the thermally excited methyl ethyl ketone were taken as fractions of the corresponding isomerization rate constant by leaving the activation energy unchanged and assigning values for the preexponential factors as to obtain the best agreement with the experimental results. (The results are not sensitive to reaction 5 and 6 individually, only to their sum.)

The Arrhenius parameters for the majority of the reactions were either estimated or copied from similar reactions in the kinetic scheme of propylene oxide decomposition.¹ Additional parameters were taken from various sources as listed in Table 5, where the main source is the NIST–Chemical Kinetics Standard Reference data base.¹⁶ The parameters for each

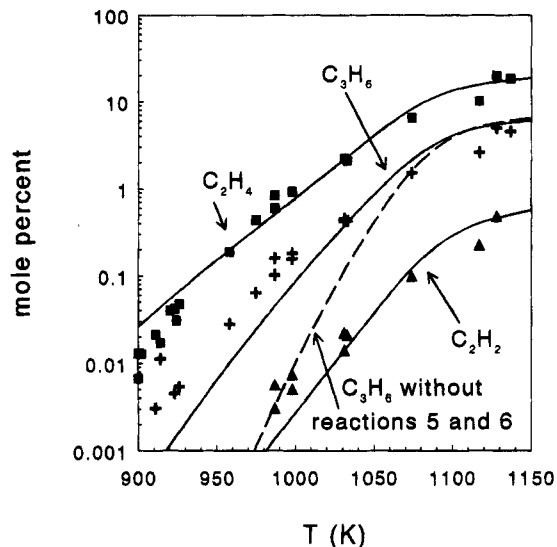


Figure 14. Experimental and calculated mole percent of acetylene, ethylene, and propylene. The dashed line in the figure shows the mole percent of propylene when the dissociation of the thermally excited methyl ethyl ketone is eliminated from the scheme.

TABLE 6: Sensitivity Analysis at 950/1100 K ($\Delta \log C / \Delta \log k$ at $t = 2 \text{ ms}$)^a

| reaction | $(\text{CH}_3)_2\text{CHCHO}$ | $\text{CH}_3\text{COC}_2\text{H}_5$ | $\text{C}_2\text{H}_5\text{—O—CH=CH}_2$ | $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{OH}$ |
|----------|-------------------------------|-------------------------------------|---|---|
| 1 | –/–0.60 | 1.01/0.47 | –/–3.32 | –/–0.92 |
| 2 | 1/0.78 | –/–0.23 | –/–0.89 | –/–0.36 |
| 3 | –/–0.15 | | –/–0.15 | 0.99/0.93 |
| 4 | | | 0.99/1.12 | |
| 22 | –/–0.30 | | | |
| 32 | | | –/–0.43 | |
| 33 | | | –/–0.94 | |

^a k is changed by a factor of 2.

reaction taken from the NIST–Kinetic data base are the best fit to a large number of entries. In view of the very large number of citations involved they are not given as references in this article. Parameters for reactions which could not be found in available compilations were estimated by comparison with similar reactions for which the rate parameters are known.

The thermodynamic properties of the species involved were taken from various literature sources.^{5,17–21} The heats of formation of several $\text{C}_4\text{H}_7\text{O}$ and $\text{C}_3\text{H}_5\text{O}$ radicals which could not be found in the present data bases were evaluated from estimated C–H and C– CH_3 bond dissociation energies in the corresponding $\text{C}_4\text{H}_8\text{O}$ isomers.

Sensitivity analysis with respect to variations (or rather uncertainties) in the estimated ΔH_f° of the above-mentioned species showed that the results of the modeling were very insensitive to the evaluated values and we have thus considered them adequate for the purpose of the modeling.

Figure 13 shows experimental and calculated mole percent of the four isomerization products. The lines are calculated at 25 K interval. These products begin to decompose at higher temperatures, particularly ethyl vinyl ether, where its allylic O– C_2H_5 bond is the weakest among all the bonds in the structural isomers.

Figures 14–17 show the experimental and calculated results for the decomposition products of 2,3-dimethyloxirane. As can be seen, the overall agreement is satisfactory.

Figures 14, 16, and 17 show also the results of a calculation (in dashed lines) for propylene, methane, and ethane, respectively, in which the direct dissociation of the thermally excited methyl ethyl ketone was eliminated from the scheme. As can readily be seen, the lines lie orders of magnitude below the experimental points. The production of free radical from this

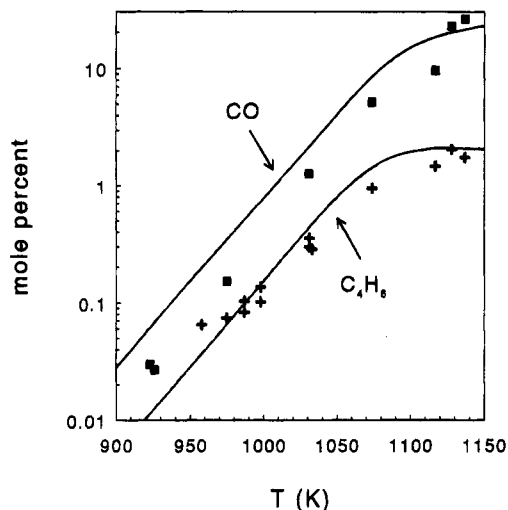


Figure 15. Experimental and calculated mole percent of butadiene and carbon monoxide.

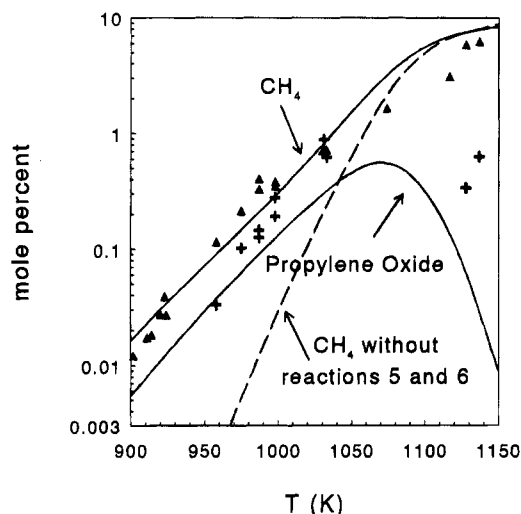


Figure 16. Experimental and calculated mole percent of propylene oxide and methane. The dashed line in the figure shows the mole percent of methane when the dissociation of the thermally excited methyl ethyl ketone is eliminated from the scheme.

reaction *must* therefore take place in this reaction system. At the higher temperature end of this study, however, the free-

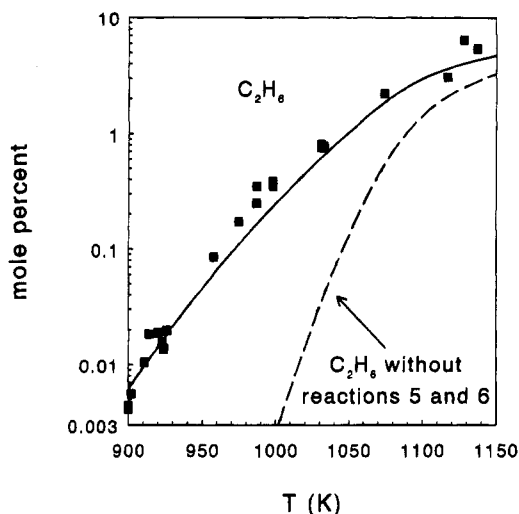


Figure 17. Experimental and calculated mole percent of ethane. The dashed line in the figure shows the mole percent of ethane when the dissociation of the thermally excited methyl ethyl ketone is eliminated from the scheme.

radical concentration level resulting from the dissociation of the cold products seems to be an important addition to the total production of free radicals. This phenomenon is more pronounced at high temperature because (1) the concentration of these products increase with temperature and (2) the process has relatively high activation energy.

Tables 6 and 7 show the sensitivity spectrum of the reaction scheme for the isomerization and the decomposition products at 950 and 1050 K respectively. The sensitivity factor S_{ij} is defined in the tables as $(\Delta \log C_i / \Delta \log k_j)$ at $t = 2$ ms. $S_{ij} = 1$ means that a factor of 2 change in k_j will cause a factor of 2 change in C_i . S_{ij} was evaluated by changing k_j by a factor of 2. Reactions that show no effect on the production rate of all the products both at high and at low temperatures were not included in the tables.

The sensitivity spectrum shown in Table 6 for the isomerization products is rather straightforward. Their production is dependent on the corresponding isomerization rates (reactions 1–4) with a sensitivity factor of approximately unity. At high temperatures, where the concentrations of free radicals in the system are high, the isomerization products decompose by free-radical attacks and become sensitive to these reactions. The

TABLE 7: Sensitivity Analysis at 950/1100 K ($\Delta \log C / \Delta \log k$ at $t = 2$ ms)^a

| reaction | CH ₄ | C ₂ H ₄ | C ₂ H ₆ | C ₂ H ₂ | C ₃ H ₆ | C ₄ H ₆ | CO | C ₃ H ₆ O | C ₂ H ₅ CHO |
|----------|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------|---------------------------------|-----------------------------------|
| 1 | -/0.14 | | | -/-0.23 | -/-0.23 | -/-0.25 | | -/-0.79 | -/-0.32 |
| 2 | -/0.33 | | | -/0.14 | 0.96/0.72 | | -/0.21 | -/-0.27 | |
| 3 | | | | 0.88/0.40 | | -/0.49 | | | |
| 4 | | | | -/0.49 | | | | -/0.48 | -/0.25 |
| 5 | 0.55/- | 0.80/0.30 | 1.09/0.56 | 0.65/0.34 | 0.55/- | | 0.86/0.32 | 0.80/0.37 | 0.82/0.29 |
| 6 | 0.12/- | 0.18/- | 0.25/0.08 | 0.14/- | 0.12/- | | 0.19/- | 0.18/- | 0.19/- |
| 8 | | | | | | | | | |
| 11 | | -/-0.15 | -/-0.27 | -0.20/-0.49 | -/-0.17 | | -/-0.18 | -0.81/-0.59 | -0.81/-0.67 |
| 12 | | | 0.19/- | | | | | 0.74/0.88 | 0.73/0.88 |
| 13 | 0.57/- | | -0.62/- | -0.20/- | -0.32/- | | | | |
| 15 | | -/0.16 | -/0.19 | -/-0.20 | | | -/0.15 | -/-0.18 | -/-0.18 |
| 16 | -/0.31 | | | | | | | | |
| 21 | | | | | -/0.23 | | | | |
| 22 | -/0.38 | | -/-0.25 | -/0.14 | 0.91/0.47 | | -/0.18 | -/0.20 | |
| 24 | | | | -/0.19 | | | | | |
| 25 | | | | 0.81/0.28 | | | | | |
| 40 | | | | | | | | -/-1.29 | 0.99/0.38 |
| 46 | | | | 0.63/0.24 | | | | | |
| 47 | | | | -0.64/- | | | | | |
| 51 | | | | -/0.21 | | | | | |
| 54 | -0.34/-0.32 | | 0.28/0.24 | -0.20/- | -0.34/-0.22 | | | | |
| 60 | | | | -0.18/-0.34 | | | | | |
| 62 | | | | 0.19/0.57 | | | | | |

^a k is changed by a factor of 2.

factor S_{ij} appears with a negative sign indicating a decrease in concentrations owing to an increase in the rate constants.

Table 7 shows the sensitivity of the decomposition products to the kinetic scheme. They are all dependent on the rate constants of the reactions that involve the decomposition of the thermally excited methyl ethyl ketone. These are reactions 5 and 6. The reactions that describe the dissociation of 2,3-dimethyloxirane and the reactions that describe the dissociation of isomers in their thermal equilibrium state at the reflected shock temperature have no or very small effect on the concentration of the decomposition products. These findings support again the assumption that the free-radical reactions are initiated by the decomposition of the thermally excited methyl ethyl ketone.

V. Conclusions

The thermal reactions of 2,3-dimethyloxirane can be summarized in the following statements:

1. The decomposition of 2,3-dimethyloxirane is a typical case of thermal activation. It begins with a bond cleavage in the thermally excited methyl ethyl ketone rather than in the reactant itself.

2. On the basis of assumption (1), a reaction scheme containing 65 elementary reactions and 41 species successfully simulated production rates and distribution of reaction products.

3. The first-order rate constants obtained in this investigation for the unimolecular isomerizations of the four isomerization reactions scatter along the corresponding Arrhenius lines extrapolated from the lower temperature data.

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