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Kinetics of the Gas-phase Thermal Decomposition of 2,3-Dimethyl-2,3-epoxypentane

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In the temperature range 638–727 K 2,3-dimethyl-2,3-epoxypentane decomposes by homogeneous, unimolecular and non-radical mechanisms to give propene, propanone, but-1-ene, *cis*- and *trans*-but-2-ene, butanone, 2,2-dimethylpentan-3-one, 3,3-dimethylpentan-2-one, 2,3-dimethylpent-1-en-3-ol, 3-ethyl-2-methylbut-3-en-2-ol and 2,3-dimethylpent-3-en-2-ol as the major products. These products arise as the consequence of seven competing primary processes and the Arrhenius parameters for each of these processes are determined. The results and conclusions of this study are in accord with those of previous studies of the thermal decompositions of other alkyl-substituted oxiranes.

Studies of the thermal decomposition of oxiranes were begun in this laboratory well over a decade ago[1] with the intention of determining the reaction pathways and the mechanisms of these reactions and as the necessary preliminary work in preparation for studies of the reactions of chemically activated oxirans to be generated by the reaction of $CH_2(^1A_1)$ with oxiranes. The aims of the thermal studies have largely been achieved[2] but it is only now, in the following paper, that we report our first study of the reaction of methylene with an oxirane (2,3-dimethyl-2,3-epoxybutane). This paper describes a study of the thermal decomposition of 2,3-dimethyl-2,3-epoxypentane which is the product expected from the insertion of $CH_2(^1A_1)$ into the C—H bonds of 2,3-dimethyl-2,3-epoxybutane. It provides data that confirm conclusions reached in previous studies of the thermal decomposition of oxiranes.[2]

EXPERIMENTAL

Kinetic studies were carried out as described previously[3] in a conventional 'static' system using two Pyrex reaction vessels. One of the reaction vessels was packed with short lengths of Pyrex tubing to give a surface-to-volume ratio (S/V) of *ca.* 12 cm^{-1} (*cf:* unpacked vessel $S/V = 1$ cm^{-1}). The reaction vessels were aged at 800 K by the pyrolysis of 10 Torr† hexamethyldisiloxane for 48 h. Young's, PTFE barrel, stopcocks were used on all parts of the vacuum system in contact with pyrolysed material and these portions of the vacuum line were heated to *ca.* 70 °C to minimise absorption problems.

Product analyses were carried out using a Perkin-Elmer 452 gas chromatograph fitted with a Pye flame ionization detector (f.i.d.) coupled to a Pye wide-range amplifier and an LDC 308 computing integrator. A 50 ft SCOT ethofat 60/25 column in series with a 50 ft SCOT didecylphthalate column at 90 °C with helium carrier gas were used for the analyses. With the exception of 3-ethyl-2-methylbut-3-en-2-ol, which was assumed to have the same sensitivity coefficient as 2,3-dimethylpent-1-en-3-ol, f.i.d. sensitivity coefficients for each of the compounds analysed were determined by injection of mixtures of known composition onto the columns. The identity of the reaction products was confirmed by g.l.c./mass spectrometry (Kratos MS 30 mass spectrometer).

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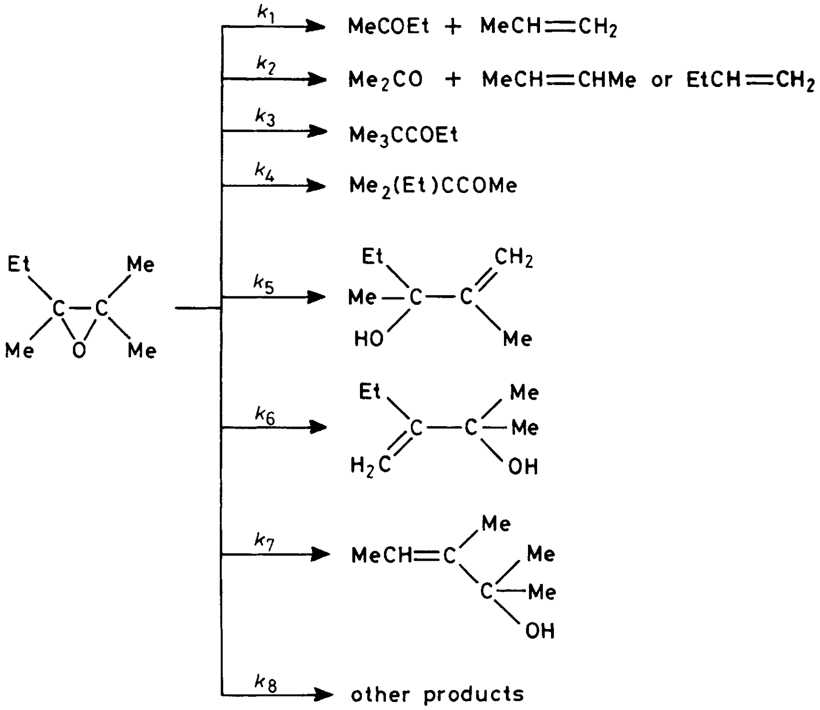
† 1 Torr = 133 N m^{-2}.

2,3-Dimethyl-2,3-epoxypentane was prepared by the method of Pasto and Cumbo[4] from 2,3-dimethylpent-2-ene and was purified to 99.9% purity by fractional distillation on a 0.6 m Podbielniak column. 3,3-Dimethylpentan-2-one and 2,2-dimethylpentan-3-one were prepared by the addition of the appropriate Grignard reagent to ethanoic or propanoic anhydride, respectively.[5] 2,3-dimethylpent-1-en-3-ol was prepared by the method of Colonge.[6] All other chemicals used were commercially available samples.

RESULTS

Pyrolysis of 2,3-dimethyl-2,3-epoxypentane (DMEP) in the temperature range 638–727 K gave propene, propanone, but-1-ene, *cis*- and *trans*-but-2-ene, butanone, 2,2-dimethylpentan-3-one, 3,3-dimethylpentan-2-one, 2,3-dimethylpent-1-en-3-ol, 3-ethyl-2-methylbut-3-en-2-ol and 2,3-dimethylpent-3-en-2-ol as major products (this list accounts for *ca.* 95% of the reaction products). The remaining minor products were methane, 3-methylpent-3-en-2-one, pentan-2-one and a few unidentified products. The ratios of propene to butanone and total butenes to propanone were unity within experimental error. The rate of loss of DMEP was found to be first order to > 50% reaction. Secondary decomposition of the major products was negligible over the range of conversions used to determine rate constants (typically not more than 20% reaction). The reactions pathways are summarised in scheme 1.



Scheme 1.

Over the pressure range 4–14 Torr at 666 K the rates of formation of the major products were independent of pressure. Nitric oxide had no effect on the yields of the major products but the yields of the minor products were reduced. The rates of

Table 1. Rate constants for the decomposition of 2,3-dimethyl-2,3-epoxypentane with an initial pressure of 8 Torr

T/ 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}	k_4/ 10^{-5} s^{-1}	k_5/ 10^{-5} s^{-1}	k_6/ 10^{-5} s^{-1}	k_7/ 10^{-5} s^{-1}
638.8	1.14	0.124	0.137	0.104	0.350	0.195	0.122	0.0665
646.8	1.82	0.228	0.247	0.171	0.546	0.295	0.194	0.0981
659.8	4.31	0.635	0.673	0.390	1.23	0.647	0.401	0.196
666.2	6.42	0.896	0.972	0.627	1.83	0.929	0.584	0.296
679.8	14.3	2.18	2.29	1.35	4.03	1.98	1.22	0.596
687.9	24.2	3.63	3.90	2.42	7.08	3.18	2.02	1.02
700.4	50.4	7.70	8.27	4.69	14.8	6.84	4.08	2.10
706.5	70.2	10.8	11.7	7.02	20.4	8.61	5.48	2.69
714.8	116	18.2	19.1	10.7	33.7	15.2	8.83	4.51
724.6	205	31.4	34.0	20.6	60.0	26.2	15.6	7.77
726.8	233	36.2	38.8	23.7	67.5	27.6	17.8	8.74

formation of the major products were identical in the packed and unpacked reaction vessels; however, the rates of formation of the minor products were higher in the packed vessel. This resulted in an increase of *ca.* 9% in the rate of loss of DMEP over that observed in the unpacked vessel.

The temperature dependence of the rate constants was investigated using the unpacked vessel with an initial reactant pressure of 8 Torr. The rate constants determined are given in table 1. In Arrhenius form the rate constants may be expressed as follows:

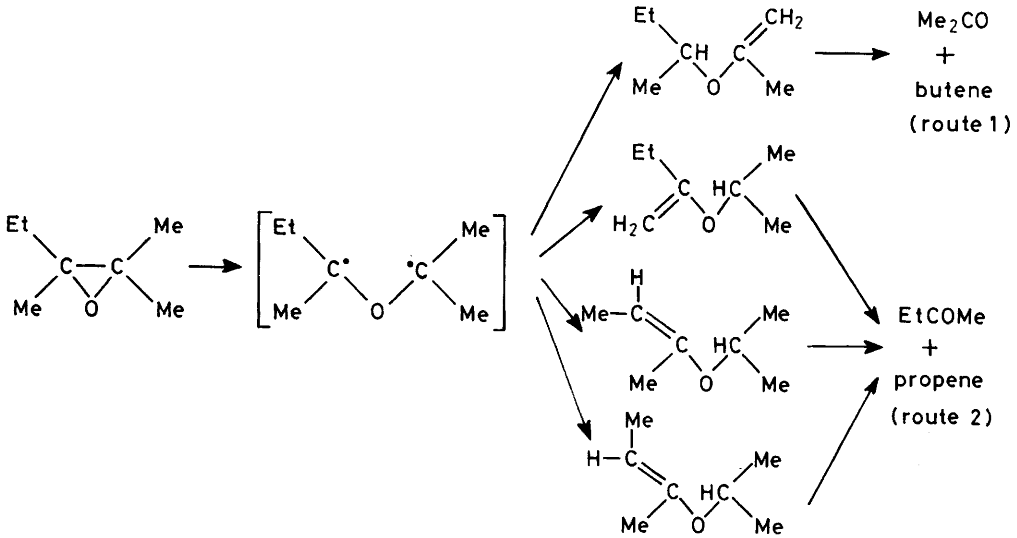
$$k_1/\text{s}^{-1} = 10^{14.25\pm0.28}\exp(-246.2\pm3.7\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_2/\text{s}^{-1} = 10^{14.23\pm0.23}\exp(-245.5\pm3.1\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_3/\text{s}^{-1} = 10^{13.41\pm0.37}\exp(-237.5\pm4.9\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_4/\text{s}^{-1} = 10^{13.56\pm0.41}\exp(-233.2\pm5.4\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_5/\text{s}^{-1} = 10^{12.29\pm0.47}\exp(-220.7\pm6.1\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_6/\text{s}^{-1} = 10^{11.93\pm0.44}\exp(-218.7\pm5.8\ \text{kJ mol}^{-1}/\boldsymbol{R}T)$$
$$k_7/\text{s}^{-1} = 10^{11.49\pm0.57}\exp(-216.9\pm7.5\ \text{kJ mol}^{-1}/\boldsymbol{R}T).$$

All error limits are statistical 95% certainty limits. Although all three straight-chain butenes were identified, their relative yields were not determined and the total yield of these products was used in the calculation of k_2. No evidence was obtained to show whether 2,3-dimethylpent-3-en-2-ol was in the (*E*) or (*Z*) forms or was a mixture of the two.

DISCUSSION

The results obtained for the thermal decomposition of DMEP are entirely in accord with the results obtained and with the mechanisms proposed for the thermal decompositions of other oxiranes previously reported.[2] The basic reactions involved are unimolecular, homogeneous and non-radical in character.

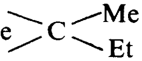
The propene, butenes, propanone and butanone arise from the initial C—C bond rupture of the oxirane ring, followed by a 1,4-hydrogen shift to give vinyl ethers which, at the temperature of the study, undergo a rapid decomposition *via* a 1,5-hydrogen shift[2, 7] (see scheme 2).



Scheme 2.

It has been suggested[2,8] that hydrogen-atom transfer in the biradical is the rate-determining step in this reaction. Our results indicate that route 2 is favoured over route 1 by a factor of 1.3 (after taking account of the differing reaction path degeneracies), and this may well be the consequence of two pathways in route 2 involving the shift of a hydrogen atom from a secondary, rather than a primary, carbon.

The ketones are presumed to result from an initial C—O bond fission of the ring to give a biradical, followed by an alkyl-group shift. If an ethyl group is assumed to transfer as readily as a methyl, then at 700 K, after correction for path degeneracy, the two ketones are found to be formed with identical rates and with virtually the same rates as observed for the ketone from 2,3-dimethyl-2,3-epoxybutane. Thus it might be argued that ethyl-group shifts are as facile as methyl shifts in these biradicals. However, it is also possible to assume that the ethyl group does not shift but the methyl group transfers more rapidly to the more substituted carbon; this tendency has been previously commented on in other oxirane systems.[3] Data for hydroperoxyalkyl radicals indicate that methyl groups migrate faster than ethyl groups by a factor of *ca.* 2 at 676 K, but that the difference in the rates becomes less at lower temperatures.[9]

It has been argued that formation of the unsaturated alcohols is a consequence of a concerted reaction from the oxirane.[2,3] For geminally dimethyl-substituted oxiranes it appears that, to account for the *A* factor change in going from mono-methyl-substituted molecules, the rotation of both methyl groups is hindered in the transition state.[2] Transfer of a hydrogen atom from one of these methyl groups to the oxygen atom results in formation of the unsaturated alcohol with relative rate constants at 700 K, after correcting for reaction path degeneracy, equal to 1.0 for 1,2-epoxy-2-methylpropane,[10] 1.0 for 2,3-epoxy-2-methylbutane,[3] 0.7 for 2,3-dimethyl-2,3-epoxybutane[2] and 0.7 for DMEP. In the present study hydrogen-atom transfer from the  $>C<^{Me}_{Et}$ group gives a value of 0.6 (hydrogen atom from the ethyl group) and 0.85 (hydrogen atom from the methyl group). Thus the results are essentially identical for all geminally dialkyl-substituted oxiranes. The mean Arrhenius parameters from these studies are $E_a = 215 \pm 5$ kJ mol^{-1} and $\log A/\text{s}^{-1} = 11.1 \pm 0.3$ (after correcting to a path degeneracy of 1); these are very close to the values of $E_a = 211$ kJ mol^{-1} and $\log A/\text{s}^{-1} = 10.9$ (11.4 per methyl group is quoted) previously quoted.[2]

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