Kinetics and Energy Transfer in the Thermal Decomposition of 2-Methyloxetane and 3-Methyloxetane

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The thermal decomposition of 2-methyloxetane and 3-methyloxetane has been studied between 660 and 760 K in the pressure range 0.01–3 kPa. In the pressure-independent range, rate coefficient expressions

 $\log(k_1^{\infty}/s^{-1}) = (14.53 \pm 0.12) - (249.2 \pm 2.2 \text{ kJ mol}^{-1})/2.303RT$

and

 $\log(k_2^{\infty}/s^{-1}) = (15.67 \pm 0.17) - (269.8 \pm 3.3 \text{ kJ mol}^{-1})/2.303RT$

were determined for 2-methyloxetane decomposition into C_3H_6 + HCHO (k_1) and C_2H_4 + CH₃CHO (k_2), respectively, while for 3-methyloxetane decomposition into C_3H_6 + HCHO (k_3) the following kinetic parameters were obtained:

$$\log(k_3^{\infty}/s^{-1}) = (15.38 \pm 0.27) - (258.7 \pm 3.7 \text{ kJ mol}^{-1})/2.303RT$$

The pressure dependence of the homogeneous decomposition rate and the efficiency of the gas-phase collisional energy transfer have been studied at 743 K. A value of $\langle \Delta E \rangle_d = 1500 \pm 300 \text{ cm}^{-1}$ was extracted from the investigation of the pressure dependence of the two-channel decomposition of 2-methyloxetane. Finally, the efficiency of the surface-gas energy transfer has been studied by the 'variable encounter method' in the range 750–1100 K. At 750 K the average energy transferred per collision with the wall was determined to be 2600 cm⁻¹ for both methyloxetanes; however, $\langle \Delta E' \rangle$ decreased considerably with increasing temperature. The results on the collision efficiencies were discussed and compared with literature data for related molecules.

The thermal decomposition of oxetanes is an important example of reactions of small-ring compounds with hetero atoms. Previous investigations of the thermolysis kinetics revealed some distinct differences in the Arrhenius parameters of oxetane^{1,2} and 3-alkyloxetanes^{3,4} on the one hand and the unsymmetrical 2-alkyl-substituted oxetanes^{5,6} on the other hand. In this paper we deal with the thermal decomposition of the two simplest representatives of these groups, *i.e.* 2-methyloxetane and 3-methyloxetane. Hammonds and Holbrook⁶ determined high-pressure Arrhenius parameters for the former, while the latter has not been studied previously.

Gas-gas and gas-wall energy-transfer efficiencies in the thermal decomposition of methyloxetanes have been studied. 2-Methyloxetane, which decomposes by two different modes and is consequently sensitive to the assumed average downward energy transfer,⁷ is particularly suitable for such investigations

Experimental

Materials

2-Methyloxetane was synthetized⁸ by ring-closure of the corresponding chloroacetate obtained from butane-1,3-diol with acetyl chloride. 3-Methyloxetane was prepared by the method of Searles *et al.*⁹ The methyloxetane samples were purified by fractional distillation on a high-performance column at atmospheric pressure, followed by several trap-totrap distillations *in vacuo*. The samples were shown to be chromatographically pure to at least 99.5%.

Homogeneous Decomposition Technique

The homogeneous decomposition procedure was similar to that described previously.¹ In most cases a cylindrical Pyrex

glass vessel of 450 cm³ volume (surface/volume ratio of 0.80 cm⁻¹) was used; however, in a few experiments the surface/volume ratio was increased to 15 cm⁻¹ by filling the reactor with short glass tubes. The reaction vessel was enclosed in an air thermostat and its temperature was controlled to within ± 0.2 K.

The pressure in the reactor was measured with a quartzspiral manometer (TEXAS Model 145). After 15–20% pressure increase the reaction was quenched by expanding the reaction mixture into a glass bulb. Product analysis was performed by g.l.c. using a 3 m Chromosorb 101 column and temperature programming from 333 to 423 K.

Variable-encounter Method

Experimental details are given in a previous publication.¹⁰ The reaction vessel was a 3 dm³ fused quartz flask equipped with three tubular reactor fingers of various sizes. The dimensions of the fingers determined the mean number of collisions, m, that a molecule entering the reactor from the 3 dm³ flask suffered with the wall before it re-emerged into the flask. Stochastic calculations¹¹ showed m to be 2.1, 3.5 and 10.5. The reactor fingers were thermostatted by electric furnaces and the inner reactor walls were 'aged' before they were put into use by pyrolysing methyloxetane in the reactor for several hours.

The reactor was carefully evacuated before each run and the required substrate pressure was made up by expanding a measured amount of gas from a smaller volume into the reactor flask. After the appropriate reaction time the reaction mixture was frozen down in a trap and the composition was determined by gas chromatography. Analysis conditions were identical with those used in the homogeneous activation system. Analytical results were used to calculate the apparent first-order rate constants, which in turn were converted¹¹

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into the mean probabilities of reaction per collision with the reactor wall, $\bar{P}_{c}(m)$.

Results and Discussion

High-pressure Rate Coefficients of the Homogeneous Thermal Decompositions of Methyloxetanes

Decomposition of 2-methyloxetane was studied in the temperature range 659-757 K at pressures above 1.4 kPa where the first-order rate coefficient proved to be pressure-independent. The extent of decomposition was varied between 5 and 25%, but this had no detectable effect on product composition. The major products were ethene, propene, formaldehyde and acetaldehyde, and the sum of the amounts of the two alkenes agreed to within 4% with that of the consumed 2-methyloxetane. This suggests the following reaction stoichiometry:

$$CH_3 CH_2: CHCH_3 + CH_2O (1)$$

$$\Box_{0}^{\dagger} \longrightarrow CH_{2}:CH_{2}+CH_{3}CHO \qquad (2)$$

Minor amounts of methane and ethane were detected; these accounted for less than 3% of the total product formation.

The overall first-order rate coefficient was calculated from the ratio of the alkene products (ethene + propene) and the unreacted 2-methyloxetane concentrations which were determined by g.l.c. Finally, the individual rate coefficients k_1 and k_2 were obtained from the overall rate coefficient and the experimental [propene]/[ethene] ratio. Arrhenius plots of the rate coefficients for propylene formation are shown in fig. 1 and least-squares fits to these data yield the expressions

$$\log(k_1^{\infty}/s^{-1}) = (14.53 \pm 0.12)$$

- (249.2 ± 2.2 kJ mol⁻¹)/2.303 RT

and

$$\log(k_2^{\infty}/\mathrm{s}^{-1}) = (15.67 \pm 0.17)$$

$$-(269.8 \pm 3.3 \text{ kJ mol}^{-1})/2.303 \text{ RT}$$

where the quoted error limits are the standard deviations.

Our experimental results show (in agreement with the findings of Hammonds and Holbrook³) that reaction (1), which forms propene and formaldehyde, is the major reaction channel in the thermal decomposition of 2-methyloxetane.



Fig. 1. Arrhenius plots for 2-methyloxetane decomposition into $C_3H_6 + HCHO(\bigcirc)$ and $C_2H_4 + CH_3CHO(\bigcirc)$.



Fig. 2. Temperature dependence of the $k_1^{\infty}/k_2^{\infty}$ ratio.

The Arrhenius parameters obtained for reaction (1) in the two investigations agree within the limits of the experimental errors. However, while in the previous investigation³ k_1^{n}/k_2^{∞} was found to be 1.31 ± 0.03 independent of temperature, the present results suggest higher ratios and indicate an increase of $k_1^{\infty}/k_2^{\infty}$ with decreasing temperature (see fig. 2). The failure to observe this temperature dependence by Hammonds and Holbrook could have been the result of the limited temperature range used in their work.

Decomposition of 3-methyloxetane was investigated between 665 and 758 K at pressures above 2.0 kPa where the first-order rate coefficients were found to be pressure independent. Propene was the only hydrocarbon detected. Gases that are not condensed at liquid-nitrogen temperature (for instance H₂ and CO) were not formed. Hence we concluded that the thermal decomposition of 3-methyloxetane followed the simple stoichiometry:

$$CH_3 \longrightarrow CH_2:CHCH_3 + CH_20 \qquad (3)$$

First-order kinetics were shown to prevail up to 60% decomposition. Rate coefficients were calculated from the g.l.c. analysis results of the pyrolysed sample. An Arrhenius plot of the data is shown in fig. 3. A least-squares fit to the results yielded the rate coefficient expression

$$og(k_3^{\infty}/s^{-1}) = (15.38 \pm 0.27)$$

- (258.7 ± 3.7 kJ mol⁻¹)/2.303 RT

where the given errors are the standard deviations.

No kinetic parameters have been published so far for the thermal decomposition of 3-methyloxetane. The Arrhenius



Fig. 3. Arrhenius plot for 3-methyloxetane decomposition.

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Fig. 4. Experimental and calculated fall-off curves for 3methyloxetane decomposition at 743 K. \bigcirc , Experimental; (----) RRKM strong-collision hypothesis; (---) RRKM stepladder model with $\langle \Delta E \rangle_d = 1500 \text{ cm}^{-1}$ and (...) $\langle \Delta E \rangle_d = 1000 \text{ cm}^{-1}$.



Fig. 5. Pressure dependence of the ratio of the two reaction pathways for 2-methyloxetane decomposition at 743 K. \bigcirc , Experimental; (----) RRKM strong-collision hypothesis; (- -) RRKM stepladder model with $\langle \Delta E \rangle_d = 900 \text{ cm}^{-1}$; (- · -) $\langle \Delta E \rangle_d = 1200 \text{ cm}^{-1}$; (· · ·) $\langle \Delta E \rangle_d = 1500 \text{ cm}^{-1}$ and (- - × -) $\langle \Delta E \rangle_d = 2000 \text{ cm}^{-1}$.



Fig. 6. Plot of $\overline{P}_{e}(m)$ versus temperature in 3-methyloxetane decomposition. Transition probability models were gaussian (----) and exponential (---) functions. $\langle \Delta E' \rangle$ values are given at five different temperatures.

parameters obtained in this work are higher than the parameters determined for the dominant route of 2methyloxetane decomposition and are similar to those reported¹ for oxetane itself.

Pressure Dependence of the Homogeneous Decomposition Rate and Gas-phase Collisional Energy Transfer

The pressure dependences of the first-order rate coefficients have been studied at 743 K between 0.01 and 2 kPa. Variation of pressure was brought about by changing the partial pressure of the methyloxetanes. Most experiments were made in the reactor without glass tubing, but the runs carried out at increased surface/volume ratio gave practically identical results.

In the evaluation of the energy-transfer efficiencies, the solution of the master equation for steady-state conditions was obtained by an iteration procedure using the algorithm developed by Tardy and Rabinovitch.¹² The transition probability matrix was constructed by assuming a stepladder model and normalizing the *i*th column to $\omega/(\omega + k_i)$, where k_i is the microscopic rate coefficient for reaction from the *i*th level and ω designates the collisional frequency. The probability matrix was operated repeatedly to an initially assumed population distribution (say to the equilibrium distribution) until the population output remained unchanged. Finally, the unimolecular rate coefficient was obtained from $k_{uni} = \sum k_i n_i^{ss} / \sum n_i^{ss}$, where n_i^{ss} is the steady-state population.

The microscopic rate coefficients for unimolecular decomposition were calculated by RRKM theory using the vibrational frequency models given in the Appendix. The collisional parameters were calculated from critical properties, thus values of s = 0.60 and 0.59 nm were obtained at 743 K for 3-methyloxetane and 2-methyloxetane, respectively.

Results for 3-methyloxetane decomposition and calculated fall-off curves for different average energies transferred per collision are shown in fig. 4. As can be seen, the theoretical results are insensitive to the assumed deactivation step size because the shift of the fall-off curves towards smaller pressures rapidly diminishes with increasing $\langle \Delta E \rangle_d$ values. Therefore, the experimental results can be described equally by the strong-collision assumption and by the stepwise collision mechanism. This behaviour is common⁷ for low-temperature thermal decompositions where the average excess energy of the reacting molecules is around the average transferred energy, and such observations have been made for instance in a study of the thermal decomposition of oxetane-2-one.¹³

The situation is basically different in case of the decomposition of 2-methyloxetane, which can react unimolecularly by two different modes. It was first recognized by Chow and Wilson⁷ and was demonstrated thereafter for several reactions that pressure-dependence studies of the unimolecular rate coefficients of multichannel thermal decompositions can supply information on the nature of the energy-transfer mechanism and on the efficiency of the gas-gas collisional energy transfer. Experimental k_1/k_2 rate coefficient ratios for 2-methyloxetane decomposition are plotted as a function of the logarithm of the collisional frequency in fig. 5. Calculated fall-off curves obtained with the strong-collision assumption as well as those derived from the stepwise deactivation mechanism are also shown. It is evident from fig. 5 that the strong-collision hypothesis is inadequate for describing the observed pressure dependence of the k_1/k_2 rate. Comparing the experiment with the theoretical curves obtained with different assumed average energies transferred per collision indicates that $\langle \Delta E \rangle_d = 1500 \pm 300$ cm⁻¹ at 743 K. There is little information in the literature on the efficiency of collisional energy transfer involving oxetanes. The present $\langle \Delta E \rangle_d$ value



Fig. 7. Plot of $\overline{P}_c(m)$ versus temperature in 2-methyloxetane decomposition. Transition probability models were gaussian (---) and exponential (---) functions. $\langle \Delta E' \rangle$ values are given at five different temperatures.

is in accordance with the average energy (transferred downward per collision) which was estimated^{10b} in a study of the thermal decomposition of oxetane (*i.e. ca.* 2000 cm⁻¹).

Surface Gas Energy Transfer

Decomposition of the oxetanes was investigated between 750 and 1100 K at *ca.* 3×10^{-2} Pa. The mean probability for reaction per collision with the reactor wall, $\bar{P}_{e}(m)$ as a function of temperature is shown on semilogarithmic plots in fig. 6 and 7 for 3-methyloxetane and 2-methyloxetane decomposition, respectively.

Theoretical simulation of a collision with the hot reactor wall was made as described by Kelley *et al.*^{11,14} The population distribution in the flask was represented by a Boltzmann population vector, and this vector was operated on by a transition probability matrix, giving a new population distribution. Then, the procedure was repeated with the new population vector (between successive wall collisions the vector was attenuated for loss due to reaction and escape from the reactor finger). Thus, a $\bar{P}_{c}(m)$ average reaction probability per collision was determined.

In the simulation of collisions with the hot wall the microscopic rate coefficient, k_i , and the model for the probability of down transition by a ΔE step were required. The k_i values were calculated by RRKM theory using the vibrational frequency models given in the Appendix, while a flat gaussian function and a flat exponential function, respectively, were used as transition probability models. The flat exponential model (E) was: $P_{\Delta E} = A_1 \exp(-\Delta E/\langle \Delta E \rangle)$ for $0 \leq \Delta E/cm^{-1} \leq 9500$ and $P_{\Delta E} = 0$ for $\Delta E > 9500 cm^{-1}$. The flat gaussian model (G) was: $P_{\Delta E} = A_2 \exp[-(\Delta E - \Delta E_{mp})^2/2\sigma^2]$ for $0 \leq \Delta E/cm^{-1} \leq 9500$ and $P_{\Delta E} = 0$ for $\Delta E > 9500 cm^{-1}$.

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Fig. 8. Temperature dependence of the ratio of reaction probabilities for two reaction pathways in the 2-methyloxetane decomposition. Transition probability models were gaussian (——) and exponential (---) functions. $\langle \Delta E' \rangle$ values are given at five different temperatures.

The results obtained with 3-methyloxetane in the three tubular reactors at various temperatures are shown in fig. 6. The theoretical curves indicated by solid lines were derived with the gaussian probability model, while the broken lines resulted from the exponential probability model; however, for both sets of calculations the average transferred energy $\langle \Delta E' \rangle$ was selected in such a way as to give the best fit to the experimental results obtained in the smallest reactor characterized by m = 2.1. With this probability matrix retained, the theoretical curves calculated for the other reactors were in very good agreement with experiment in the case of the gaussian model; however, significant deviations occurred in the case of the exponential model. This means that the transition probabilities are much better represented by the flat gaussian function.

2-Methyloxetane decomposes thermally by two reaction channels. The results obtained for the temperature dependence of the overall decomposition probabilities are presented in fig. 7. Again, the flat gaussian model gives a much better representation of the transition probabilities than the exponential one. This difference in the applicability of the two transition probability models is even more marked in fig. 8, where the ratios of decomposition probabilities *via* channels 1 and 2 are plotted against the temperature. It is perhaps noteworthy to draw attention to the fact that the theoretical $\vec{P}_c(m)_1/\vec{P}_c(m)_2$ ratios, which agree very well with experiment, were obtained with a flat gaussian transition probability model corresponding to a $\langle \Delta E' \rangle$ value which was fitted to the experimental temperature dependence of the $\vec{P}_c(2.1)$ overall decomposition probability.

In wall collisions of energized methyloxetane molecules, a considerable increase of deactivation efficiency is found with decreasing temperature. Towards low temperatures, the methyloxetanes behave in gas-surface interactions like strong colliders. Similar tendencies have been observed in previous VEM (variable encounter method) studies of small-ring hydrocarbon decompositions,^{10a,15,16} and the inverse trend was shown to be in accordance with the results obtained from a quasi-statistical accommodation model.¹⁷ However, the negative temperature coefficient of $\langle \Delta E' \rangle$ found for the decomposition of oxetanes appears to be somewhat larger than that reported for cycloalkane decompositions (see also table 1). Verification of this observation and its explanation requires further investigation.

Table 1. Comparison of $\langle \Delta E' \rangle$ values for different molecules

decomposing molecule		$\langle \Delta E' \rangle / \mathrm{cm}^{-1}$				
	$E_0/\text{kJ} \text{ mol}^{-1}$	800 K	900 K	1000 K	1100 K	ref.
cyclopropane	267.8		2400	2100	2000	15
cyclobutane	263.6		2125	1925	1875	16
oxetane	259.4	2970	2660	2400	2200	10a
3-methyloxetane	247.4	2570	2260	2000	1790	this work
2-methyloxetane	239.8 ^a	2460	2150	1890	1680	this work

^a The given E_0 refers to reaction (1), while $E_0 = 259.1 \text{ kJ mol}^{-1}$ for reaction (2).

The average energies transferred per collision with the wall which were determined so far are summarized in table 1 and are compared with similar properties of small-ring hydrocarbon compounds. The results for the decomposition of the oxetanes support the earlier observations¹² made in the studies of cycloalkanes and other compounds, namely that the energy-transfer efficiency in wall collisions decreases with increasing complexity of the colliding molecule. Taking this trend into account, one tends to conclude (in spite of the limited amount of information available) that the energytransfer efficiency of the oxetanes in surface-gas collisions is higher than that of the corresponding cycloalkanes. The higher energy-transfer efficiency for the more polar oxetanes is not unreasonable since one expects them to exert stronger interactions with the surface than do the cycloalkanes.

Finally, in the case of 2-methyloxetane we can compare the energy-transfer efficiencies in gas-wall and gas-gas collisions. At 750 K the average energy transferred per collision with the wall is $\langle \Delta E' \rangle = 2600 \text{ cm}^{-1}$, while the transferred energy per gas-phase collision is $\langle \Delta E \rangle_d = 1500 \text{ cm}^{-1}$. This means that at low temperatures methyloxetane is a strong collider in gas-wall collisions and is a much less efficient collider in gas-gas collisions. However, taking into account the strong inverse temperature dependence of the energy-transfer efficiency of the wall ellisions and the probably much smaller temperature dependence in the gas-phase collisions, one expects methyloxetane to behave as a weak collider.

Appendix

Frequency Model for Methyloxetane Molecules

The vibrational frequency models for methyloxetane molecules were deduced from the oxetane molecular frequencies¹ by taking into account the substitution of an H atom with a CH₃ group. The common frequency model for 2-methyloxetane and 3-methyloxetane after grouping was: 2947 (8), 1437 (6), 1312 (2), 1172 (4), 1036 (6), 941 (3), 370, 200 (2) and 90 cm⁻¹.

Activated Complex Models

The reaction coordinate was a 1036 cm⁻¹ ring frequency. A 1312 and a 1172 cm⁻¹ twisting frequency was lowered until the calculated A factor reproduced the experimental one.

Activated complex 1: 2947 (8), 1437 (6), 1312, 1172 (3), 1036 (5), 941 (3), 440, 380, 370, 200 (2) and 90 cm⁻¹. $E_0 = 239.7$ kJ mol⁻¹.

Activated complex 2: 2947 (8), 1437 (6), 1312, 1172 (3), 1036 (5), 941 (3), 370, 200 (2), 110 (2) and 90 cm⁻¹. $E_0 = 259.1$ kJ mol⁻¹.

Activated complex 3: 2947 (8), 1437 (6), 1312, 1172 (3), 1036 (5), 941 (3), 370, 220, 200 (2) and 90 cm⁻¹. $E_0 = 247.4$ kJ mol⁻¹.

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