# Thermolyses of 2-Methyloxetan and 2,2-Dimethyloxetan

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The thermolysis of 2-methyloxetan has been reinvestigated at temperatures between 429.5 and 483.2 °C and initial reactant pressures from 6.0 to 14.2 Torr. Two parallel unimolecular reactions occur producing either propene and formaldehyde or ethene and acetaldehyde. The ratio of propene to ethene is  $1.31 \pm 0.03$  within this temperature range. The total rate constant for disappearance of reactant is given by

 $\log_{10}(k/s^{-1}) = (14.89 \pm 0.36) - (249.8 \pm 4.7 \text{ kJ mol}^{-1})/2.303 \text{ RT}.$ 

The thermolysis of 2,2-dimethyloxetan was studied in the same apparatus at temperatures between 402.2 and 471.3 °C and at reactant pressures from 7.2 to 9.2 Torr. The reactant disappears by two parallel unimolecular paths to give either isobutene and formaldehyde or ethene and acetone. Minor products of methane, propene and isobutane were also detected. The ratio of isobutene to ethene was found to differ considerably from unity and to be strongly temperature-dependent. The following rate expressions were derived for the overall rate of disappearance of reactant  $(k_{2,2})$  and for the rate constants for the individual reactions producing isobutene  $(k_3)$  and ethene  $(k_4)$ 

 $\log_{10}(k_{2,2}/s^{-1}) = (13.78 \pm 0.24) - (226.0 \pm 2.7 \text{ kJ mol}^{-1})/2.303 \text{ RT}$   $\log_{10}(k_3/s^{-1}) = (13.48 \pm 0.25) - (222.1 \pm 2.9 \text{ kJ mol}^{-1})/2.303 \text{ RT}$  $\log_{10}(k_4/s^{-1}) = (15.56 \pm 0.34) - (270.6 \pm 4.4 \text{ kJ mol}^{-1})/2.303 \text{ RT}.$ 

The differences observed between the thermolyses of these two compounds are noted and compared with previously obtained results for other methyl-substituted oxetans. A possible explanation for the difference in Arrhenius parameters for the two paths in the case of the 2,2-disubstituted compound is suggested.

Recent work on the thermolysis of 2-ethyloxetan<sup>1</sup> has revealed some differences in the Arrhenius parameters for the reactions of oxetans substituted in the 2- and 3-positions. In order to extend the comparison we decided to re-examine the thermolysis of 2-methyloxetan for which only the unpublished data of Cohoe<sup>2</sup> and of Shirazi<sup>3</sup> existed previously and also to examine the effect of *gem* di-substitution. The compound 2,2-dimethyloxetan has not been studied previously, nor are there any detailed results for other compounds *gem*-substituted in the 2-position, although Searles<sup>3</sup> has commented on the low rate of decomposition of 2,2-diethyloxetan in comparison with oxetan itself.

# **EXPERIMENTAL**

The sample of 2-methyloxetan used in most of this work was kindly given to us by Dr M. Bartok (University of Szeged, Hungary) and was found to be > 99.0% pure by g.l.c. Identical results were obtained in some runs using a commercial sample (Aldrich Chemical Co. Ltd, stated purity 98%) which was distilled under vacuum before use. 2,2-Dimethyloxetan was prepared by ring closure of the corresponding bromoalcohol using tributyl tin ethoxide. After an initial fractional distillation, the product was purified by preparative g.l.c. to > 99% purity.

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# THERMOLYSES OF METHYL-SUBSTITUTED OXETANS

#### APPARATUS

The apparatus and procedure were similar to that described previously.<sup>1</sup> A Pyrex glass vessel was used with a surface/volume ratio of  $1.08 \text{ cm}^{-1}$  and volume 269 cm<sup>3</sup>. The dead volume was 13.6 cm<sup>3</sup> and this was taken into account in calculating rate constants. The vessel was packed with lengths of glass tubing for some experiments. This produced a surface/volume ratio of 11.6 cm<sup>-1</sup> and volume of 147.6 cm<sup>3</sup>. Methane, ethene, propene and isobutene were determined by g.l.c. using a 12 ft column of Chromosorb P coated with 14% bis-2-methoxyethyladipate plus 7% di-2-ethylhexylsebacate, operated at 60 °C. Tests for CO and H<sub>2</sub> were made using a 6 ft molecular sieve column and helium carrier gas. Minor products were also analysed using A Perkin-Elmer Sigma 1 g.l.c. system containing a 7 ft Durapak C column (phenyl isocyanate on Porasil C). The reaction was followed by pressure changes monitored by an S.E.L. pressure transducer type 1150 D.

## RESULTS

### 2-METHYLOXETAN

Thermolysis experiments with 2-methyloxetan were carried out in the reaction vessel seasoned with hexamethyl disilazane. The major products were found to be ethene, acetaldehyde, propene and formaldehyde as would be expected from the two reactions (1) and (2):

$$CH_3 \longrightarrow CH_2 = CH - CH_3 + CH_2 0$$
(1)

The overall pressure change was found to correspond closely to the sum of the amounts of propene and ethene formed at all temperatures, thus confirming the stoichiometry.

The thermolysis obeyed first-order kinetics up to 70% reaction, as can be seen from a typical log plot shown in fig. 1. The first-order rate constants were found to be independent, within experimental error, of initial pressure (up to 47 Torr), of added nitric oxide (up to 11%) and of the surface/volume ratio of the vessel (increased by a factor of 10.7) (see table 1).

A series of 75 runs at initial pressures normally in the range 7-9 Torr was carried out between 483 and 429.5 °C to derive the Arrhenius parameters. The data obtained are given in table 2. Where multiple runs were done at a single temperature the rate constants quoted are average values with a standard deviation of typically  $\pm 1$ %.

The following rate expression was derived, where the error limits represent the 95% confidence limits:

$$\log_{10}(k/s^{-1}) = (14.89 \pm 0.36) - (249.8 \pm 4.7 \text{ kJ mol}^{-1})/2.303 \text{ RT}.$$

The ratio  $k_1/k_2$  was found from the observed ratio of propene/ethene. A mean value of  $1.31 \pm 0.03$  was found from a total of 56 measurements made over the temperature range 426-477 °C. Minor products of methane, ethane and propane were detected by g.l.c.

## 2,2-DIMETHYLOXETAN

The expected modes of decomposition of 2,2-dimethyloxetan would be according to reactions (3) and (4):

$$(CH_3)_2 = CH_2 + CH_2 O$$
(3)

$$\begin{array}{c} 1 & \text{ch}_3 \\ \hline 0 & \text{ch}_3 \\ \text{ch}_3 \\ 2 \\ \text{co} & + \\ \text{c}_2 \\ \text{H}_4 \end{array}$$
 (4)

		effec	t of initi	al pressu	re		
	T/⁰C	$P_0/1$	ſorr	$k/10^{-4}$	s <sup>-1</sup> k	$/10^{-4} \text{ s}^{-4}$ (calc.) <sup><i>a</i></sup>	-1
	458.7	7.	01	11.78		11.60	
	458.6	13.	06	11.82		11.54	
	458.7	25.	30	11.54	ļ	11.61	
	458.4	47.	37	11.60	)	11.41	
		effect	of added	nitric ox	ide		
						k	$/10^{-4} \text{ s}^{-1}$
<i>T/</i> °C	Ì	P <sub>0</sub> /Torr	% N	0	k/10 <sup>-4</sup> s <sup>-</sup>	1	$(calc.)^a$
458.8		8.12	5.7	7	11.17		11.67
458.7		7.86	10.6	5	11.21		11.61
458.4		7.57	11.2	2	10.23		11.41
	efi	fect of pack	ed vessel	(S/V =	11.6 cm <sup>-1</sup>	)	
		-			k	/10 <sup>-4</sup> s <sup>-</sup>	-1
	<i>T/</i> °C	$P_0/1$	forr	$k/10^{-4}$	S <sup>-1</sup>	(calc.) <sup>a</sup>	
	444.5	7.	01	5.06	,	5.15	
	444.6	7.	11	4.83		5.18	
	444.1	7.	04	4.67	,	5.03	
	444.1	6.	94	4.71		5.03	
	444 1	7	30	4 92	i.	5.03	

TABLE 1.—EFFECT OF VARIATION OF CONDITIONS ON THE THERMOLYSIS OF 2-METHYLOXETAN

<sup>a</sup> Calculated from the observed rate expression for the reaction in the absence of nitric oxide in the unpacked vessel  $(S/V = 1.08 \text{ cm}^{-1})$ .

TABLE 2.—RATE CONSTANTS FOR THE THERMOLYSIS OF 2-METHYLOXETAN

T/°C	483.2	482.4	477.0	476.8	470.4	470 3	459 1
$k/10^{-4} \text{ s}^{-1}$	42.86	41.86	32.45	34.47	21.17	20.98	9.89
Ť∕°C	458.8	458.7	458.6	458.5	458.4	458.3	458.2
$k/10^{-4} \text{ s}^{-1}$	11.17	11.59	10.38	11.53	11.20	11.15	12.01
T/°C	457.6	457.4	457.3	457.2	446.8	446.7	446.6
$k/10^{-4}  \mathrm{s}^{-1}$	10.77	10.31	10.70	10.94	5.567	5.498	5.570
T/°C	446.5	446.4	446.3	446.2	446.0	445.8	439.6
$k/10^{-4} \text{ s}^{-1}$	5.601	5.975	5.110	5.407	5.228	5.099	3.809
T∕°C	439.5	439.0	430.2	430.1	429.7	429.5	
$k/10^{-4} \text{ s}^{-1}$	3.858	3.941	2.223	2.261	2.236	2.294	

The overall stoichiometry was confirmed by the fact that the total pressure increase was found to be equal, within experimental error, to the sum of the isobutene and ethene pressures as measured by g.l.c. The overall reaction [according to steps (3) and (4)] followed by pressure change was first order up to ca. 70% decomposition, as can be seen from fig. 2. The first-order rate constants were independent, within experimental



FIG. 1.-First-order plot for 2-methyloxetan thermolysis at 458.2 °C.



FIG. 2.-First-order plot for 2,2-dimethyloxetan thermolysis at 471.1 °C.

error, of initial pressure (up to ca. 40 Torr) and of added nitric oxide (up to 15%) (see table 3). On carrying out the thermolysis in the packed vessel, a small increase in rate constant occurred which can be attributed to a small heterogeneous contribution to path (3) which amounts to 1-2% in the unpacked vessel.

		effect of init	tial pressur	e at 445 °C		
$P_0/\text{Torr}$ $k_{2,2}/10^{-3} \text{ s}^{-1}$	8.03 2.241	14.61 2.210	18.26 2.300	23.02 2.256	30.33 2.219	41.20 2.310
		effect of	added nitr	ic oxide	· · · · · · · · · · · · · · · · · · ·	
					$k_{2,2}/10^{-1}$	4 s <sup>-1</sup>
<i>T</i>	Г/°С	$P_0/\text{Torr}$	% NO	$k_{2,2}/10^{-4} \text{ s}^{-1}$	<sup>1</sup> (calc.)	) <sup>b</sup>
41	9.6	8.00	5.0	5.300	5.53	32
41	8.1	8.54	7.5	5.300	5.300 5.08	
41	9.5	8.78	9.8	5.400 5.50		00
418.3		8.77	10.3	5.100	5.100 5.13	
418.2		8.61	15.1	5.100	5.100 5.10	
		effect of packed	vessel (S/	$V = 11.6 \text{ cm}^{-1}$		
		_			$k_{3}(\text{calc.})$	
<i>T/</i> °C	$P_0/\text{Torr}$	$k_{2,2}/10^{-4} \text{ s}^{-1}$	R <sup>a</sup>	$k_3/10^{-4} \text{ s}^{-1}$	$/10^{-4} \mathrm{s}^{-1b}$	$\% k_3$ het. <sup>c</sup>
443.6	8.11	24.0	42.7	23.45	19.84	1.9
443.6	7.55	24.3	41.8	23.73	19.84	2.0
443.6	8.73	23.7	40.4	23.13	19.84	1.7
443.6	7.42	23.7	43.0	23.16	19.84	1.7
443.6	8.77	23.2	42.4	22.67	19.84	1.5
442.9	7.34	24.8	44.3	24.25	19.13	2.7
443.0	7.51	24.5	37.5	23.86	19.23	2.5
443.0	7.27	23.5	42.0	22.95	19.23	1.9

TABLE 3.—EFFECT OF VARIATION OF CONDITIONS ON THE THERMOLYSIS OF 2,2-DIMETHYLOXETAN

<sup>a</sup>  $R = k_3/k_4$ . <sup>b</sup> Calculated from the appropriate rate expression for the unpacked vessel.  $^{c}$  heterogeneous contribution to path (3) calculated from

$$\frac{[k_3 - k_3 \text{ (calc.)}] \ 1.08 \times 100}{10.52 \ k_3 \text{(calc.)}}$$

The Arrhenius parameters were obtained from a total of 42 runs in the temperature range 402-471 °C and at pressures from 7.2 to 9.2 Torr. The data for these are presented in table 4. The value of R (the ratio of isobutene to ethene from g.l.c.) at each temperature was used to calculate the individual rate constants  $k_3$  and  $k_4$  from the overall rate constant  $k_{2,2}$ .

The results are summarised by the following rate expressions:

$$\log_{10}(k_{2,2}/s^{-1}) = (13.78 \pm 0.24) - (226.0 \pm 2.7 \text{ kJ mol}^{-1})/2.303 \text{ }RT$$
  

$$\log_{10}(k_3/s^{-1}) = (13.48 \pm 0.25) - (222.1 \pm 2.9 \text{ kJ mol}^{-1})/2.303 \text{ }RT$$
  

$$\log_{10}(k_4/s^{-1}) = (15.56 \pm 0.34) - (270.6 \pm 4.4 \text{ kJ mol}^{-1})/2.303 \text{ }RT.$$

## THERMOLYSES OF METHYL-SUBSTITUTED OXETANS

T∕°C	471.3	471.1	471.0	458.3	457.9	457.7
$k_{2}/10^{-4} \text{ s}^{-1}$	80.77	81.16	80.92	45.54	44.72	45.68
T/°C	457.4	447.2	447.1	447.0	438.7	438.4
$k_{2} / 10^{-4}  \mathrm{s}^{-1}$	44.91	26.01	25.41	25.63	15.30	15.05
T/°C	430.5	430.3	418.6	418.5	418.4	418.0
$k_{2}^{2}/10^{-4} \text{ s}^{-1}$	10.32	9.720	5.175	5.203	5.145	5.236
$T/^{\circ}C$	411.0	410.9	410.7	403.8	402.8	402.3
$k_{2}/10^{-4} \text{ s}^{-1}$	3.399	3.171	3.370	2.154	2.156	2.136
$T/^{\circ}C$	402.2					
$k_{2,2}/10^{-4} \text{ s}^{-1}$	2.128					

## TABLE 4.—RATE CONSTANTS FOR THERMOLYSIS OF 2,2-DIMETHYLOXETAN

Small amounts of methane, propene and isobutane were detected by g.l.c. From the shape of the appearance/time curves for these products it is clear that isobutane is a secondary product and that methane and propene are produced in part by secondary processes.

# DISCUSSION

The thermolysis of 2-methyloxetan has been confirmed to proceed mainly by the unimolecular paths (1) and (2). The overall Arrhenius parameters are in agreement, within experimental error, with those found previously by Cohoe,<sup>2</sup> who reported a lowering of the rate constants by 6-7% in the presence of nitric oxide. This effect was not noted in our work, although a small amount of the minor product methane could possibly have arisen by a primary process involving free radicals. This, however, never constituted > 3% of the total products. The ratio of the amounts of propene and ethene formed was  $1.31 \pm 0.03$ , invariant with temperature. Cohoe reported a similar lack of temperature dependence and a slightly higher ratio (1.50). The Arrhenius parameters for 2-methyloxetan are very similar to those reported for 2-ethyloxetan<sup>1</sup> and show a lowering of both A and E parameters in comparison with 3-substituted compounds.

The thermolysis of 2,2-dimethyloxetan was investigated principally to study further the effect of substitution at the 2-position in the oxetan ring and to seek an explanation for the effect of such substitution upon the observed Arrhenius parameters. The observed rate constants are compared with those of analogous cyclobutane compounds in table 5. In most cases it is seen that the oxetans decompose more slowly than the corresponding cyclobutanes, but the 2,2-dimethyl compound is an exception. The effect is large and difficult to reconcile with the observation of Searles<sup>4</sup> concerning the 2,2-diethyl compound. In table 6, the Arrhenius parameters for 2,2-dimethyloxetan show a marked contrast with those for the mono-substituted oxetans. There is in this case a definite predominance of the path producing the more highly alkylated olefin [isobutene, path (3)] and a strong temperature dependence of the ratio  $k_3/k_4$  was observed which is reflected in the difference in Arrhenius parameters for paths (3) and (4). It is seen that in comparison with the other substituted oxetans, the Arrhenius parameters for path (3) are low whereas those for path (4) resemble the 'normal' values associated with oxetan itself and the 3-substituted compounds. The kinetic features of the thermolysis of both oxetan and 2-ethyloxetan can be reconciled with a biradical mechanism similar to that proposed for the decomposition of cyclobutanes. 'Bensontype' calculations for the probable biradical intermediates involved in the thermolysis

oxetan	$k/10^{-4} \text{ s}^{-1}$	ref.	cyclobutane	$k/10^{-4} \text{ s}^{-1}$	ref.
	4.71	5		5.18	8
	( <i>a</i> ) 4.02 ( <i>b</i> ) 3.06	this work		8.07	9
	( <i>a</i> ) 2.70 ( <i>b</i> ) 2.34	1		7.33	10
cis	(a) 2.06 (b) 4.01	6	cis	17.7	11
trans	(a) 1.78 (b) 2.24	6	trans	9.56	12
	17.5	7	$\square$	18.6	13
$\square_{\circ}^{\prime}$	( <i>a</i> ) 27.7 ( <i>b</i> ) 1.04	this work			

TABLE 5.—Comparison of rate constants for oxetans and cyclobutanes at 450  $^{\circ}C^{a}$ 

<sup>a</sup> Path (a) leads to the more highly alkylated olefin and path (b) leads to the less highly alkylated olefin.

of 2.2-dimethyloxetan cannot however explain the large difference between the rates of the two reaction paths for this compound. In particular, the observed activation energy for path (3) is lower than the estimated heat of formation of the probable biradical intermediate. A possible alternative explanation could be that path (3) occurs by a concerted rather than a biradical process. The normal concerted decomposition of oxetan in company with the reverse suprafacial addition of ethene and formaldehyde would be symmetry forbidden.<sup>14</sup> An allowed process, although normally expected to be of higher energy, would be the addition of ethene to formaldehyde via a twisted conformation, producing suprafacial attack at one carbon atom and antarafacial attack at the other. The reverse process, *i.e.* the decomposition, could in principle proceed via such a distorted transition state. Normally it would be expected that this process could not compete with the biradical mechanisms. There are, however, reasons for believing that the concerted process could occur for the 2,2-disubstituted compound in the case of path (3). These can be most easily seen in terms of the frontier orbital theory applied to the cycloaddition of the aldehyde and olefin. Fleming<sup>15</sup> has discussed in detail the effect of alkyl substitution on the HOMO and LUMO energies of the molecules involved. In principle, one should consider all possible HOMO/LUMO interactions but the most important in the case of olefin/carbonyl compound reactions are likely to be those of the HOMO of the carbonyl compound with the LUMO of the olefin. The minimum energy separation

compound	$\log_{10} (A_a/s^{-1})$	$\log_{10} (A_b/\mathrm{s}^{-1})$	$E_a/kJ$ mol <sup>-1</sup>	$E_b/\mathrm{kJ}$ mol <sup>-1</sup>	(k <sub>a</sub> /k <sub>b</sub> ) 450 °C	ref.
	14.64	14.52	249.8	249.8	1.31	this work
	14.20	14.14	246.5	246.5	1.15	1
	15.24	15.70	261.5	254.5	0.510	6
	15.49	15.91	255.4	270.5	0.720	6
$\square \land \circ$	13.48	15.56	222.1	270.6	26.6	this work
	(15.71)		(263.7)		(1.00)	5

TABLE 6.—ARRHENIUS PARAMETERS AND RATE CONSTANT RATIOS FOR THERMOLYSES OF UNSYMMETRICAL OXETANS

LUMO (carbonyl) – HOMO (olefin), and hence the maximum rate enhancement, is achieved when the LUMO (carbonyl) energy is lowered and the HOMO (olefin) energy is raised. Increased methyl substitution in the olefin (by increasing the electron density) is likely to have this effect, hence the concerted addition of isobutene to formaldehyde is favoured over that between ethene and acetone. By microscopic reversibility the decomposition path (3) would similarly be favoured over path (4) if these were concerted processes. Similar arguments have recently been advanced by Imai and Nishida<sup>16</sup> to explain product ratios found in the thermolysis of 3-alkyl-2-phenyloxetans. In this system as in theirs it may be that concerted and biradical processes occur concurrently, but clearly the biradical mechanism alone cannot explain the observed experimental facts. We are currently examining other substituted oxetans to clarify these matters. Some preliminary molecular orbital calculations (carried out by Dr D. F. Ewing) have confirmed the general conclusions concerning the energies of the orbitals concerned.

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