Kinetics of the Thermal Gas-phase Decomposition of 2-Butoxypropene

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Summary: The kinetics of the thermal gas phase decomposition of 2-butoxypropene has been studied over the temperature range 640-680 K at pressure between 10 and 50 torr. 1-Butene and acetone were the only products and accounted for 63% of butoxypropene decomposition. These products are formed by homogeneous, unimolecular pathways with high pressure first order rate constant given by the equation:

$k_d/S^{-1} = 10^{10.80 \pm 0.24} \exp(-171.3 \pm 2.9 \text{ KJ mol}^{-1}/RT)$

A six membered polar transition state is consistent with the kinetics data.

Introduction

Although there are number of thermal gas phase decomposition studies of aliphatic ethers, there have been few examples in these studies of vinyl ethers with a substituent on the vinyl carbon. 2-(1-methyl-ethoxy)propene and 2-ethoxypropene are the only ethers of this type to have been studied previously [1,2].

Thermal reactions of aliphatic ethers are known to proceed through a retro-ene molecular mechanism via six membered cyclic transition states [3-7]. However, more recent detailed studies of ethoxyethene by Y.T. Lee [8] and 2-ethoxypropene by I.A. Awan and M.C. Flowers [2] showed the presence of radical pathways in competition with intramolecular rearrangement mechanisms.

The investigation of the kinetics of the thermal gas phase decomposition of 2-butoxypropene was carried out as it is a vinyl ether with a substituent on the vinyl carbon.

Results and Discussion

The kinetics of the thermal gas phase decomposition of 2-butoxyopropene were studied in the temperature range 640-680 K. Acetone and 1-butene were the only products. A typical chromatogram is shown in Figure 1.

$CH_2=CO(CH_3)\text{-}(CH_2)_3\text{-}CH_3 \rightarrow (CH_3)_2CO + CH_2=CH\text{-}CH_2\text{-}CH_3$

First order rate plot for the loss of 2-butoxypropene using 30 torr. initial pressure was linear to ca. 63%. (see Fig. (2)). The rate constants based on the loss of initial reactant were obtained at six temperatures and are listed in Table-1. The Arrhenius dependence of the rate constants is given by:

$k_d/S^{-1} = 10^{10.80 \pm 0.24} \exp(-171.30 \pm 2.90 \text{ KJ/mol}^{-1}/RT)$

Table-1: Rate constants for 2-butoxypropene decomposition at 30 torr initial pressure.

Temp./K	$k_{total}/10^{-5}$ S^{-1}
680	423
672	299
666	229
659	167
646	91
640	62

Error limits are statistical 95% certainty values.

The effect of surface on the reaction was investigated at 680 K using the packed reaction vessel. Kinetics runs were carried out in both packed and unpacked reaction vessels with a pressure of 30 torr and pyrolysis time of 15 minutes. The overall rate of reaction proceeded 44% faster than the unpacked reaction vessel. Evidently, there is some surface reaction occurring; but assuming the extent of this reaction is proportional to the S/V ratio for

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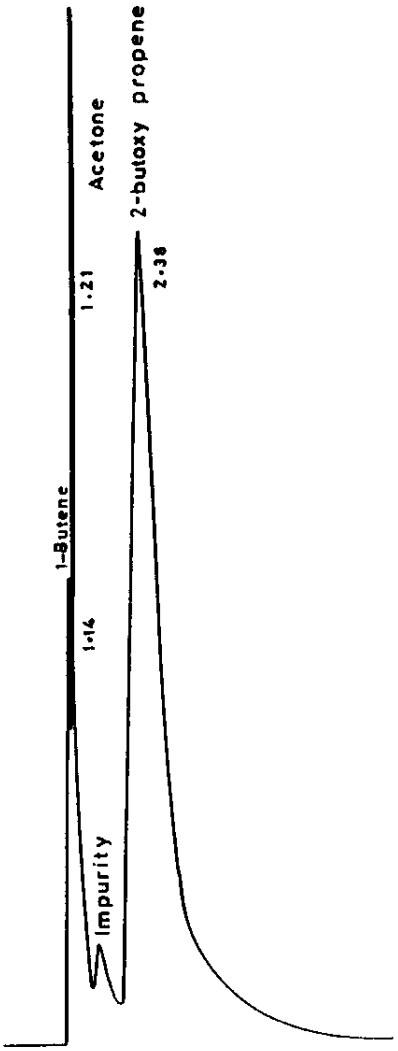


Fig. 1: A typical pyrogram from the pyrolysis of 2-butoxy propene at 685 K. (30 torr initial pressure).

the reaction vessels, the surface reaction constitute only 3.6% of the overall reaction rate in unpacked vessel.

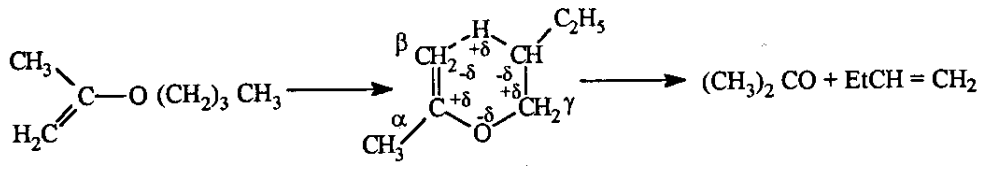
The effect of changes of pressure on the reaction rate were studied at 680 K (Table-2). Total rate of decomposition was found to decrease with decrease in pressure. This behavior could well be due to the normal unimolecular fall off. No correction to the Arrhenius parameters was attempted.

Table-2: Pressure dependance of reaction rate for decomposition of 2-butoxypropene at 680 K.

Temp./K	$k_{total}/10^{-5}$ S^{-1}
10	410
20	412
30	422
40	427
45	423
50	425

The decomposition of 2-butoxypropene to acetone and 1-butene has been shown to be the result of first order, homogeneous, non-radical and presumably, unimolecular reactions. The formation of acetone and 1-butene can be explained in terms of a concerted mechanism via a six membered cyclic transition state analogous to one proposed for other vinyl ether; these involved some ionic character (Scheme-1).

The charge separation in the corresponding ester is more pronounced. The calculation made by Richard & O'Neal [9] on vinyl ethers decomposition revealed that charge stabilization per methyl group for vinyl ether would be 7 KJ mol^{-1} compared with 14 $KJmol^{-1}$ for the corresponding esters. Flowers and Honeyman [1] on the basis of their experimental results for the thermolysis of 2(1-methyl methoxy)-propene observed a reduction of 10 $KJmol^{-1}$ in the activation energy for methyl substituent on carbon atom. However, Awan and Flowers [2] in their study of thermal decomposition of 2-ethoxypropene could not observe any decrease in activation energy corresponding to methyl stabilization. Values previously determined for the alkyl vinyl ethers are shown in Table-3.



Scheme-1

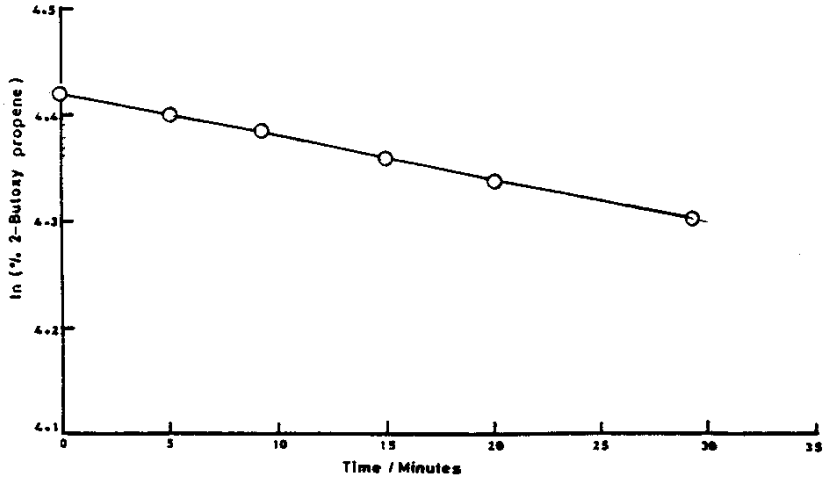


Fig. 2: First order rate plot for the loss of 2 butoxy proepene at 646 K. (30 torr inital pressure)

Table-3: Alkyl vinyl ethers decomposition

Reactant	Product	log k/s (600 K)	log A/S	Ea/KJ mol.	Ref.
CH_2=CHOCH$_2$Me	CH_2=CH_2 + MeCHO	-4.53	11.43	183	4
		-4.52	11.60	186	3
		-4.34	11.47	182	7
CH_2=CHO(CH$_2$)$_2$Me	MeCH=CH_2+MeCHO	-4.82	11.49	187	12
CH_2=CHOCHMe$_2$	MeCH=CH_2+MeCHO	-3.39	12.12	178	12
		-3.31	12.58	182	13
CH_2=CHOCHMe$_3$	Me_2C=CH_2 + MeCHO	-2.33	10.86	151	12
		-1.99	12.00	161	7
CH_2=CHOCH (Cl)Me	CH_2=CHCl+MeCHO	-4.82	11.50	187	12
CH_2=C(Me)OCHMe$_2$	MeCH=CH_2+Me_2CO	-2.65	11.98	168	1
CH_2=C(Me) OCH$_2$Me	CH_2=CH_2=Me_2CO	-3.59	12.50	185	2
CH_2=CHO(CH$_2$)$_3$Me	EtCH=CH_2+MeCHO	-4.29	11.15	177	14
CH_2=C(Me)O (CH$_2$)$_2$Me	EtCH=CH_2+Me_2CO	-4.10	10.80	171	This work

Comparison of activation energy of 171 KJmol^{-1} for 2-butoxypropene with that of butoxyethene (cf. 177 KJmol^{-1}) indicates a decrease in activation energy by 6 KJmol^{-1} which is consistent with the charge stabilization effect of methyl substitution at vinylic carbon.

It has been proposed in previous studies that there is a high energy direct fragmentation pathway to form an alkyl radical. This fragmentation pathway would have an activation energy of about 225 KJmol^{-1} and is not of any significance under the conditions of this study. This is borne out by the absence of any other product resulting from free radical pathways except 1-butene and acetone in the reaction mixtures.

A comparison of the rate constants of 2-butoxypropene with butoxyethene at 600 K shows the former reaction to be 1.5 times faster. This increase in rates is lower than that found for 2-ethoxypropene compared with ethoxyethene. Flowers and Honeyman [1] in their investigation of thermal gas phase decomposition of 2-(1-methyl ethoxy) propene observed that thermal decomposition proceed 5 time faster than (1-methyl ethoxy)ethene. The increase in the rate was explained in terms of a reduction of 10kJmol^{-1} in activation energy due to substitution at carbon atom. Similar observation had been made by Awan and Flowers [2] in their study of the kinetics of thermal gas phase decomposition of 2-ethoxypropene. The small effect on the rate of 2-butoxypropene of methyl substitution could be due to

unexpected low A factor in the present work. Although there is no apparent reason for such deviation.

Experimental

Kinetics studies were carried out in a conventional static vacuum system with two pyrex reaction vessels [10]. One of the reaction vessel was packed with short lengths of pyrex tubing to give a surface to volume ratio S/V 12 cm^{-1}, the other was of similar external dimensions but not packed (S/V ca. 1 cm^{-1}, volume ca. 100 cm^3). The reaction vessels were aged prior to kinetic studies by pyrolysis of 30 torr. of hexamethyldisiloxane at 683 K for 24 hours. Greaseless stopcocks were used in all parts of the vacuum line in contact with the pyrolysed material. Reaction vessels were immersed in a fused salt ($NaNO_3/NaNO_2/KNO_3$ ternary eutectic) thermostate, the temperature of which was maintained to ± 1°C by AOC - AW temperature controller. Temperature was measured with a Ni-Cr-Ni thermocouple.

Analyses were carried out by gas chromatography using a Shimadzu GC-7 AG gas chromatograph and a 30 m x 0.25 mm squalane WCOT column maintained at 30°C. A flame ionisation detector coupled to a Spectra Physics model SP-4600 data Jet integrator was used for quantitative determination of the eluted compounds. The identification of reaction products were confirmed from comparison of retention time with those of standards.

2-Butoxypropene was prepared in two steps from 2,2-dimethoxypropane, first by ketal exchange and then acid elimination by the method of N.B. Lorette and W.L. Howard [11]. The product was purified to 77% by fractional distillation on a podbielniak column followed by preparative GLC using a thermal conductivity detector. The identity of the compound was confirmed by infrared spectroscopy.

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