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

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Summary: Kinetics of the gas phase decomposition of 2-ethoxypropene has been studied over the temperature range 544-635 °K at a pressure between 3 and 72 torr. Ethene and propanone, formed in equimolar amount (± 4 %), were the major products and accounted for ≥ 04% of the total reaction. These products are formed by homogeneous, non-radical, unimolecular pathways with the high pressure rate constant given by the equation:

$$k_d/S^{-1} = 10^{12.51\pm0.25} \exp(-184.6 \pm 2.8 \text{ KJ mol}^{-1}/RT)$$

The other products identified were n-butane, 2-methylprop-2-enal, butanone and 2-pentanone in ratios of approximately 0.01 : 0.015 : 0.03 : 0.07 relative to ethene respectively. The kinetics and mechanims for the formation of these products are discussed in detail.

Introduction

The thermal decomposition of many aliphatic ethers has been reported previously and found to proceeds through a retro-ene molecular mechanism via six membered cyclic transition states [1-5]. However a more recent detailed study of the decomposition of ethoxyethene by Y.T. Lee [6] et al, using an infrared multiphoton absorption technique showed the presence of radical pathways in competition with intramolecular rearrangement mechanism.

The investigation of the kinetics of the thermal gas phase decomposition of 2-ethoxypropene was carried out as it is a vinyl ether with a substituent on the vinyl carbon.2-(1-methyl -ethoxy) propene is the only other ether of this type to have been studied previously [7]. The kinetics and the mechanism for the formation of various products of the thermal gas phase decomposition of 2-ethyoxypropene has been examined in detail in this study.

Experimental

Pyrolyses were carried out as described previously [8] in a conventional "Static" system using Pyrex reaction vessels aged prior to kinetic runs by pyrolysis of approximately 20 torr hexamethyldisiloxane at 520°C for 24-48 h. Two reaction vessels were used. One was packed with short lengths of Pyrex tubing to give a surface to volume ratio (S/V)≈ 13 cm^{-1}, the other was of similar external dimensions but was not packed (S/V Ca. 1 cm^{-1}, volume Ca. 150 cm^3). Young's greaseless stopcocks were used in all parts of the vacuum system in contact with pyrolysed material.

Analyses were carried out by gas chromatography using a 50 m squalane SCOT column maintained at Cá. O°C with helium carrier gas. A pye flame ionization detector coupled to a Pye

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wide range amplifier and an LDC 308 computing integrator was used for quantitative determination of the eluted compounds. The detector sensitivity coefficients for ethene and propanone relative to 2-ethyoxypropene were determined by injection of known composition on the chromatographic column. The identification of the reaction products was confirmed from retention times and by gas chromatography/mass spectrometry (Kratos MS 30 mass spectrometer).

The 2-ethoxypropene (b.p. 61.9°C) was prepared from decomposition of β-ethoxycrotonic [9] acid at 160-165°C. The product was purified to >99.9% by fractional distillation on a 0.6 m Podbielniack type column. Other chemicals used were commercially available samples.

Results

The kinetics of the thermal gas phase decomposition of 2-ethoxypropene was studied in the temperature range, 544-535 °K. Ethene and propanone, formed in equimolar amounts (± 4%) were the major products and accounted for > 94% of the total reaction. The other products indentified were n-butane, 2-methylprop-2-enal, butanone and 2-pentanone in ratios of approximately 0.01:0.015 : 0.013 : 0.07 relative to ethene respectively.

The effect of nitric oxide (10%) on the reaction was studied at 566 and 620 K. The total rate of loss of 2-ethoxy-propene was decreased approximately 10% but the rate of formation of ethene and propanone was unaffected. An interesting feature of this study was the total elimination of the products other than ethene and propanone. This clearly indicated the presence of a competitive radical pathway for the decomposition of 2-ethoxypropene in addition to the intramolecular rearrangement reaction.

First order plots for the loss of 2-ethoxypropene using 30 torr initial pressure was linear to greater than 65% reaction (see figure 1). The rate constants based on the ethene yield (this product gave the more consistent results) were obtained at six temperature and listed in Table 1. The Arrhenius dependence of the rate constants is given by:

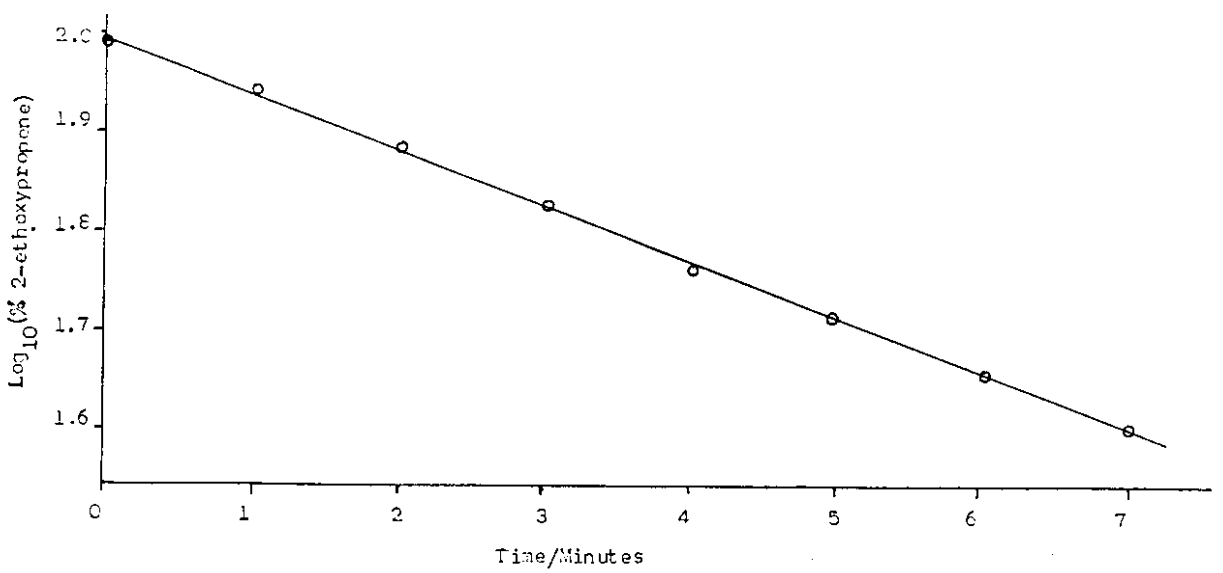


Fig.1: First order rate plot for the loss of 2-ethoxypropene at 635 °K (30 Torr initial pressure).

$k_d/s^{-1} = 10^{12.51\pm0.25} \exp(-184.6\pm2.8 KJ\ mol^{-1})/RT$

Error limits are statistical 95% certainty values. The effect of surface on the reaction was investigated at 620 K using a packed reaction vessel. Within the experimental errors the rate of reaction was the same in packed and unpacked reaction vessels. The effect on reaction rate of varing the total pressure betwen 3 and 72 torr was studied at 602 K. The total rate constant was found to increase slightly with increase in pressure (See Table 2). This could well be due to the normal unimolecular fall-off. However, as the effect of pressure was small no corrections to the Arrhenius parameters were attempted.

Table-1: Rate constants for the decomposition of 2-ethoxypropene at 30 Torr initial pressure.

Temp/K	$k_{total}/10^{-5}\ s^{-1}$
635.1	221
619.6	93.8
602.4	32.6
589.5	15.0
566.1	3.18
544.1	0.63

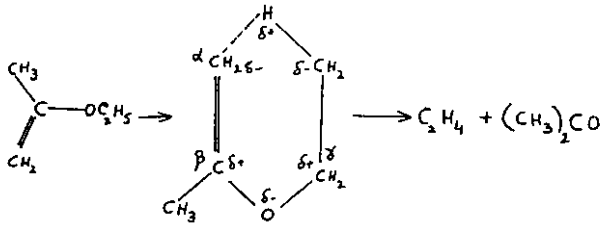
Table-2: Pressure dependence of reaction rate for the decomposition of 2-ethoxypropene at 602.4K

Pressure/Torr	$k_{total}/10^{-5}\ s^{-1}$
3	3.22
6	3.30
7	3.41
13	3.41
20	3.44
31	3.50
46	3.55
60	3.60
72	3.69

Discussion

a. Formation of ethene and propanone

The formation of these compounds can be explained in termsof a concerted mechanims involving a transition state analogous to one proposed for other vinyl ethers; these involed some ionic character.



Scheme-I

The charge separation in the corresponding decomposition of alkyl ester is more pronounced. The calculation made by Richard and O'Neal [10] on vinyl ether decomposition revealed that charge stabilization per α methyl group for vinyl ethers would be 7 KJ $mole^{-1}$ compared with 14 KJ $mole^{-1}$ for the corresponding esters. Recently M.C. Flowers and M.R.Honeyman [7] on the basis of their experimental results for the thermolysis of 2(-1-methyl-methoxy)-propene concluded that methyl substitution on the α carbon had the same charge stabilization effect as when on α carbon atom. They observed a reduction of 10 KJ mol^{-1} in the activation energy. Values previously determined for the decomposition of alkyl vinyl ethers are shown in table 3.

A comparison of the rate constants of 2-ethoxypropene with ethoxy-ethene at 600 °K shows the former reaction to be 10 times faster. This increase is about the same as found for isopropyl vinyl ether compared with ethoxyethene, indicating that α and γ carbons in the transition state have similar charge densities, thus supporting

Table-3: Alkyl Vinyl ethers decomposition

Reactant	Products	log k/s^{-1} (600°K)	log A/s^{-1}	Ea/K J $mole^{-1}$	Reference
CH_2=CH-OCH_2Me	CH_2=CH_2+MeCHO	-4.53	11.43	183	2
		-4.52	11.60	186	1
		-4.32	11.47	182	5
CH_2=CH-$OCHMe_2$	MeCH=CH_2+MeCHO	-3.39	12.12	178	a
		-3.31	12.58	182	b
CH_2=C(Me)$OCHMe_2$	MeCH=CH_2+Me_2CO	-2.65	11.98	168	7
CH_2=C (Me)OCH_2Me	CH_2=CH_2+Me_2CO	-3.59	12.5	185	This work.

a. T.O.Bunkole and E.U.Emovan, J.Chem.Soc., B, 1968, 332.
b. A.T.Blades, Can.J.Chem. 1953, 31, 418.

the earlier work. However, the corresponding reduction in the activation energy is not apparent. This may be due to the large uncertainties involved in the studies of ethoxyethene or the unexpected higher A factor in the present work. Although there is no apprent reason for such deviation.

b. Fragmentation Products

The formation of n-butane, 2-methylprop-2-enal, 2-butanone and 2-pentanone was confirmed by G.C./mass spectrometry analysis and by injecting authentic samples. A radical chain pathway initiated by the homolytic fission of the C-C bond or C-O of the ethyl group of 2-ethoxypropene seems to be the most likely cause for these products. The total elimination of these products in the presence of 10% nitric oxide supports the radical pathway. The absence of a surface effect on the total rate of loss of 2-ethoxypropene suggests that the chain termination reaction is predominantly homogeneous. Comparison of the molecule with ethyl vinyl ether suggests that the lowest energy initiation step is

$$CH_2 = C(CH_3)O\ C_2H_5 \longrightarrow CH_2 = C\ (CH_3)\text{-}O + C_2H_5 \quad (1)$$

The activation energy for the above process has been reported as 275 kJ $mole^{-1}$. This is consistent with the present work on 2-ethoxypropene.

The following mechanism is proposed for the formation of these products:

$$CH_2 = C(CH_3)O\text{-}C_2H_5 \xrightarrow{1} (CH_3)_2CO + C_2H_4$$

$$2 \downarrow (A)$$

$$CH_2 = C\ (CH_3)O\text{-}CH_2 \longrightarrow CH_2{=}C(CH_3)CHOH + H$$

$$+CH_3$$

$$H + CH_2{=}C(CH_3)OC_2H_5 \xrightarrow{3} (CH_3)_2C\text{-}OC_2H_5 \longrightarrow (CH_3)_2CO + C_2H_5$$

$$CH_3 + CH_2{=}C(CH_3)OC_2H_5 \xrightarrow{4} C_2H_5C(CH_3)OC_2H_5 \longrightarrow CH_3CC_2H_5 + C_2H_5$$

$$C_2H_5 + CH_2{=}C(CH_3)OC_2H_5 \xrightarrow{5} C_3H_7C(CH_3)OC_2H_5 \longrightarrow C_3H_7OCH_3 + C_2H_5 \quad (P)$$

$$2C_2H_5 \xrightarrow{6} n\text{-}C_4H_{10}$$

Scheme-II

The steady state concentration of the radicals are

$$[CH_3]_{ss} = \frac{K_2}{K_4} \qquad 1$$

$$[H]_{ss} = \frac{K_2}{K_3} \qquad 2$$

$$[CH_2H_5]^{\frac{1}{2}}_{ss} = \left(\frac{K_2\,[A]}{K_6}\right)^{\frac{1}{2}} \qquad 3$$

The rate of formation of 2-pentanone (P) is then given as

$$\frac{d[P]}{dt} = K_5 \left(\frac{K_2}{K_6}\right)^{\frac{1}{2}} [A]^{3/2}$$

Where K_2, K_5, K_6 represent the rate constants corresponding to various processes in Scheme (2). [A] is the concentration of substrate after time t. Similarly the rate of formation of 2-butanone can be represented as

$$d[B]/dt = K_2 [A] \qquad 5$$

but $[A] = [A]_o e^{-\Sigma k t}$ where $[A]_o$ is the initial concentration of 2-ethoxypropene and Σk represents the first order rate constant for the total loss of 2-ethoxypropene. Therefore the first order rate law based on propanone yield is given as

$$\frac{[P]}{[A]_o} = 2/3 \frac{k_5}{\Sigma k} \left(\frac{k_2}{k_6}\right)^{\frac{1}{2}} [A]_o^{\frac{1}{2}} \left[1-\left(\frac{[A]}{[A]_o}\right)^{3/2}\right] \quad (6)$$

Plot of $[P]/[A]_o$ against $[[A]_o]^{3/2}$ were made for the six temepratures. All the plots were linear and from the slopes of these plots the value of

$$\frac{K_5}{\Sigma k} \left(\frac{k_2}{k_6}\right)^{\frac{1}{2}} (dm^3\ mole^{-1})^{\frac{1}{2}} = k_{means.}$$

were calculated

Due to lack of kinetics data for the individual processes shown in scheme (2) the mean value of Arrhenius parameters were estimated from the slope of the plot of $\log_{10} k_{meas.}$ against 1/T (where T is temperature in K). Thus the mean value of Arrhenius parameters based on 2-pentanone yield are

$$E_{mean} = E_5 - E_{\Sigma k} + \tfrac{1}{2} E_2 - \tfrac{1}{2} E_6 \quad 4 \text{ kJ mole}^{-1}$$

$$\log_{10} A_{mean}/dm^3\ mole^{-1} sec^{-1} = \log A_5 - \log A_{\Sigma k} + \tfrac{1}{2} \log A_2 - \tfrac{1}{2} \log A_6 \quad 0.5$$

where the subscript of E and A represents the various processes in Scheme (2). Similarly, the mean value for Arrhenius parameters based on 2-butanone yield were.

$$E_{mean} = E_2 - E_{\Sigma k} \simeq 19 \text{ kJ mole}^{-1}$$

$$\log A_{mean}/dm^{-3} mole^{-1} sec^{-1} = \log A_2 - \log A_{\Sigma k} = -0.5$$

Table-4: Arrhenius parameters for some free radical reactions.

Process	log A/s^{-1}	E_a/kJ mole^{-1}	Reference
$CH_2=C(CH_3)OC_2H_5 \xrightarrow{2} CH_2=C(CH_3)OCH_2+CH_3$	12.0	306[a]	This work
		203[b]	
$C_2H_5+A \xrightarrow{5} CH_3CH_2CH_2CCH_3+C_2H_5$	9.5	30 (assumed)	1
$C_2H_5+C_2H_5 \xrightarrow{6}$ n-butane	10.0	0	2
$CH_2=C(CH_3)OC_2H_5 \xrightarrow{1} (CH_3)_2CO+C_2H_4$	12.5	184	This work

a. Value based on 2-propanone yield.

b. Value based on 2-butanone yield.

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From the known Arrhenius parameters for the processes 1,6 and the estimated values of process 5, one can estimate the Arrhenius parameters for process (2), i.e. the fission of CH_2-CH_3 bond. The calculated Arrhenius parameters are shown in Table 4.

A comparison of activation energy for the fission of CH_2-CH_3 bond with the estimated value of 355 kJ $mole^{-1}$ by Y.T.Lee et al [6] showed that the present value of 306 is low. Also the arrhenius "A" factor for the process (5), i.e. addition of C_2H_5 radical to substrate should not be greater than 10^8 dm^3 $mole^{-1}$ s^{-1}. The calculated value of 9.5 is thus high. The A factor for process (2) is very low. Thus, although there are a number of inconsistencies in the present kinetic data, they do provide a semi-quantitative analysis of the proposed reaction mechanism. It is quite possible that alternative reactions also contribute to the reaction pathways thus invalidating the present interpretation of the Arrhenius parameter.

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