The Thermal Decomposition of Alkyl Vinyl Ethers. Part III.[1] Maximally Inhibited Decompositions of n-Propyl, Isobutyl, and 2-Methoxyethyl Vinyl Ethers

By **Titus O. Bamkole**, Chemistry Department, University of Ibadan, Ibadan, Nigeria

Pyrolyses of n-propyl, isobutyl, and 2-methoxyethyl vinyl ethers have been carried out in a static system in the temperature range 653—708 K. The pyrolyses are homogeneous first-order reactions yielding acetaldehyde and an alkene. The Arrhenius equations (i)—(iii) were obtained. The results are discussed in terms of a six-membered

$$\text{2-methoxyethyl: } \log (k/\text{s}^{-1}) = 11{\cdot}14 \pm 0{\cdot}09 - (184{\cdot}9 \pm 1{\cdot}2\ \text{kJ mol}^{-1}/2{\cdot}303RT) \qquad \text{(i)}$$

$$\text{n-propyl: } \log (k/\text{s}^{-1}) = 11{\cdot}12 \pm 0{\cdot}13 - (177{\cdot}9 \pm 1{\cdot}7\ \text{kJ mol}^{-1}/2{\cdot}303RT) \qquad \text{(ii)}$$

$$\text{isobutyl: } \log (k/\text{s}^{-1}) = 10{\cdot}58 \pm 0{\cdot}08 - (174{\cdot}5 \pm 1{\cdot}0\ \text{kJ mol}^{-1}/2{\cdot}303RT) \qquad \text{(iii)}$$

cyclic transition state and corroborate our earlier finding that the rate-determining step of the reactions is primarily alkyl–oxygen bond polarisation rather than bond-making between a β-hydrogen atom and the terminal vinyl carbon.

PREVIOUSLY [1,2] we reported the pyrolytic decomposition of n-butyl, t-butyl, isopropyl, and 2-chloroethyl vinyl ethers. Our results supported a mechanism involving a six-membered cyclic transition state first proposed for the pyrolysis of alkyl vinyl ethers by Rice and Teller [3] and which Maccoll [4] supported by analogy with the mechanism for the pyrolysis of alkyl esters. The results of previous investigations [1,2,5-7] make possible an assessment of the effect of α-methylation of the alkyl portion and of one electron-withdrawing β-substituent, in good agreement with the proposed mechanism. This paper reports the effect of β-methylation and of another electron-withdrawing group (methoxy) in the β-position of the alkyl portion.

EXPERIMENTAL

Isobutyl vinyl ether (Koch–Light) and 2-methoxyethyl vinyl ether (K and K) were fractionated. The fractions with b.p. 356·2—357·2 K (lit.,[8] 356·2 K) and 380·2 K (lit.,[9] 380·2 K) respectively were used. n-Propyl vinyl ether was prepared by the transetherification method of Watanabe and Conlon [9] using n-propyl alcohol and isodecyl vinyl ether. The fraction, b.p. 338·2 K, n_D^{22} 1·383, was used. Cyclohexene (B.D.H.) was treated with sodium sulphite, dried, and distilled. The fraction, b.p. 356·2 K, was used. Purity was established by g.l.c.

The apparatus was a conventional static system coupled to a Mitronic Micro Comparator and a Smith's Servoscribe potentiometric recorder for automatic recording of pressure variation in the reaction vessel. The vessel was embedded in an electrically heated aluminium block and its temperature was controlled by a Versicon type 101 temperature controller to within ±0·2 K. The reactions were carried out by distilling the reactants (known pressures of cyclohexene and the appropriate vinyl ether) into the vessel which had been previously seasoned with the products of the decomposition of allyl bromide and recording the pressure variation automatically over the first 50% of reaction. Rate constants were determined by the initial rates method, and compared in a number of cases with the values obtained over the first 50% of reaction by the integral method. Good agreement was obtained.

The products were analysed by g.l.c. using a benzyldiphenyl on Celite column. Acetaldehyde was also determined by treating the frozen-out run product with a stock solution of standard sodium bisulphite and back-titrating the unchanged sodium bisulphite against standard alkali.

RESULTS AND DISCUSSION

In the absence of cyclohexene, the decompositions of n-propyl, isobutyl, and 2-methoxyethyl vinyl ethers in a seasoned vessel were fast. When cyclohexene was present, the rate decreased to a lower reproducible value which is associated with the molecular component of mixed molecular and free-radical mechanisms in which maximal suppression by cyclohexene has eliminated the free radical component. This maximally inhibited reaction was studied in both packed and unpacked vessels. The surface : volume ratio of the packed vessel was increased ten-fold by packing the vessel with pieces of Pyrex glass tubing. For each compound, the rate constants obtained in the packed and unpacked vessels are the same within experimental error. The absence of an induction period for the maximally inhibited reaction and the lack of significant variation of the rate constants with varying pressures of cyclohexene (Table 1) probably showed complete exclusion of any chain component and consequently the reactions are essentially homogenous and molecular.

G.l.c. showed the products over the first 50% of reaction were as expected: acetaldehyde and either propene, isobutene, or methyl vinyl ether. The extent of reaction measured by pressure increase is in good agreement with the titrimetric estimation of acetaldehyde. Therefore, and in agreement with our earlier reports, the

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stoicheiometry (1) was assumed where R is an alkyl radical with β-hydrogen atoms.

$$CH_2{=}CHOR \longrightarrow CH_3CHO + \text{olefin} \qquad (1)$$

First-order rate constants k were calculated from the initial slope of the pressure–time curve by means of equation (2) where P_0 is the initial pressure of the vinyl

$$k = P_0^{-1}(dp/dt)_0 \qquad (2)$$

ether and also, in a large number of cases, by the integral method. Good first-order rate constants, independent of P_0 were obtained (Table 1).

TABLE 1

Independence of the rate constants k of the initial pressure P_0, of the reactant with varying ratios of $P_0 : P_c$ where P_c is the pressure of cyclohexene

Isobutyl vinyl ether at 676·6 K								
P_0/Torr *	102·6	174·0	207·0	264·0	227·0	161·0	113·0	
$P_0 : P_c$	0·36	0·54	0·78	1·0	1·57	3·29	4·04	
10^3k/s^{-1}	1·38	1·24	1·29	1·21	1·36	1·43	1·40	
P_0/Torr *	317·0	430·0						
$P_0 : P_c$	7·38	7·55						
10^3k/s^{-1}	1·31	1·39						
n-Propyl vinyl ether at 665·0 K								
P_0/Torr *	60·0	107·0	122·0	115·0	103·0	99·0	201·5	285·0
$P_0 : P_c$	0·29	0·41	0·54	0·99	1·75	2·06	3·76	4·67
10^3k/s^{-1}	1·11	1·15	1·13	1·13	1·21	1·18	1·20	1·18
P_0/Torr *	215·0	267·0	146·0					
$P_0 : P_c$	5·25	6·22	6·35					
10^3k/s^{-1}	1·22	1·12	1·14					
2-Methoxyethyl vinyl ether at 685·6 K								
P_0/Torr *	270·0	286·0	300·0	340·0	488·0	520·0	622·0	
$P_0 : P_c$	0·63	1·19	1·35	1·43	1·18	2·01	2·64	
10^3k/s^{-1}	1·11	1·17	1·14	1·14	1·12	1·10	1·16	

* 1 Torr = 133·3 N m^{-2}.

The Arrhenius parameters for the variation of rate constants with temperature (Table 2) are given by equations (3)—(5) (error limits are standard errors).

$$\text{2-Methoxyethyl: } \log(k/\mathrm{s}^{-1}) = 11{\cdot}14 \pm 0{\cdot}09 - (184{\cdot}9 \pm 1{\cdot}2\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT) \qquad (3)$$

$$\text{n-Propyl: } \log(k/\mathrm{s}^{-1}) = 11{\cdot}12 \pm 0{\cdot}13 - (177{\cdot}9 \pm 1{\cdot}7\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT) \qquad (4)$$

$$\text{Isobutyl: } \log(k/\mathrm{s}^{-1}) = 10{\cdot}58 \pm 0{\cdot}08 - (174{\cdot}5 \pm 1{\cdot}0\ \mathrm{kJ\ mol^{-1}}/2{\cdot}303RT) \qquad (5)$$

An inspection of the Arrhenius parameters reported above together with those for 2-chloroethyl,[1] ethyl,[7] and n-butyl [2] vinyl ethers shows that electron-withdrawing β-substituents cause an increase of activation energy relative to the ethyl derivative while electron-releasing β-substituents cause a decrease. This fact and also the qualitative sequence of the activation energy values are fully compatible with a mechanism in which partial C–O polarisation contributes significantly to the rate-determining step. However, the effect of β-substituents is small compared with the similar effect of α-substituents.

TABLE 2

Variation of rate constants with temperature

2-Methoxyethyl vinyl ether							
T/K	666·1	666·9	678·3	685·6	687·5	706·7	
No. of runs	3	4	5	7	7	8	
10^4k/s^{-1}	4·5	4·6	7·7	11·3	12·4	30·2	
n-Propyl vinyl ether							
T/K	648·5	654·9	668·7	675·2			
No. of runs	7	6	11	5	6		
10^4k/s^{-1}	5·9	8·0	13·5	15·6	20·1		
T/K	679·4	685·6	691·2	697·0			
No. of runs	4	7	5	11			
10^4k/s^{-1}	24·4	32·4	46·9	58·8			
Isobutyl vinyl ether							
T/K	655·0	666·2	677·8	683·7	686·0	699·0	700·8
No. of runs	7	5	7	3	3	3	8
10^4k/s^{-1}	4·6	7·7	12·9	16·4	20·1	34·9	36·0

The much lower value of the pre-exponential factor A for the case of isobutyl vinyl ether (incidentally in good agreement with the estimated value, log A 10·65, using the method of O'Neal and Benson [10]) is probably associated with the smaller number of β-hydrogen atoms in this compound than the others and therefore with the smaller number of configurations in which the β-hydrogen atom is suitably disposed to effect an electrophilic attack on the terminal carbon atom of the vinyl portion. A similar effect has been observed for the same reason in the pyrolysis of acetates by Scheer [11] and Maccoll.[12]

In conclusion, it might be said that the very large negative entropies of activation and the relative activation energy values recorded here for the pyrolyses of β-substituted alkyl vinyl ethers corroborate our earlier views [1] on the mechanism of the pyrolysis of alkyl vinyl ethers, *i.e.* the involvement of a six-membered cyclic transition state in which alkyl–oxygen bond polarisation is substantially rate determining.

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