The Thermochemical Kinetics of the Retro-' ene ' Reactions of Molecules with the General Structure (Allyl)XYH in the Gas Phase. Part X.[1] Unimolecular Thermal Decomposition of Diallyl Ether

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The gas-phase thermal decomposition of diallyl ether (DAE) was investigated in the temperature range 545—627 K. The reaction yields acrolein and propene as the only products and appears to be a homogeneous, unimolecular process. First-order rate constants (determined using the internal standard technique) were insensitive to a 15-fold change in surface : volume ratio, the extent of conversion, and the addition of 5·8-fold excess of toluene or hex-1-ene. The rate constants were also invariant over a 13-fold variation in initial DAE pressure and were found to fit the Arrhenius relationship (i). Conversions obtained on the basis of the products agree with those using the internal

$$\log (k_1/\text{s}^{-1}) = (11{\cdot}83 \pm 0{\cdot}13) - (40{\cdot}90 \pm 0{\cdot}35\ \text{kcal mol}^{-1})/2{\cdot}3RT \qquad \text{(i)}\ ‡$$

standard method. The thermal decomposition of DAE fits into the general context of retro-' ene ' reactions involving a concerted [1,5] shift *via* a six-centre transition state as found for but-3-enols, but-3-enoic acids, and allylamines.

RECENT studies of the thermal decomposition of various *N*-alkyl-*N*-allylamines [1-5] and hepta-1,6-diene [6] have shown that these reactions occur *via* a concerted, six-centred transition state, *i.e.* by a retro-' ene ' mechanism analogous to that for butenoic acids,[7] butenols,[8] and allyl ethers.[9] As shown in the preceding paper,[1] a significant rate accelerating effect may take place which is interpreted by invoking the stabilization of a polar transition state. In this paper we investigate the extent of an analogous effect for allyl ethers.

EXPERIMENTAL

Materials.—Diallyl ether (DAE) (99·98%), obtained from Fluka, was distilled before use. Tetrahydrofuran (THF) (99·66%), Merck, was used as one internal standard and heptane (H) (99·35%), UCB, as the other.

Two mixtures of starting material and tetrahydrofuran or heptane were made up in molar ratios of DAE/THF = 0·8416 (A) and DAE/H = 1·242 (B) respectively. The two mixtures were kept in a closed vessel and portions were removed by syringe through a medicinal septum.

Reagent grade toluene and hexene, used as diluents, were obtained from UCB and Fluka respectively.

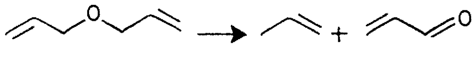
Apparatus and Procedure.—The experiments were carried out in the reaction system described in the preceding paper [1] and essentially the same procedure was used except for the work-up. In the majority of the experiments, the reaction mixture was condensed into a spherical bulb and allowed to vaporize. After *ca.* 1 h at room temperature, the mixture was analysed by g.l.c. using direct gas injection. In 13 out of 42 experiments, a different work-up was employed. After condensation of the reaction mixture at 77 K, the low molecular weight, volatile products were distilled at 173 K and the residue then condensed into a small vial. G.l.c. analysis was then carried out *via* liquid injection. When this method was employed, only DAE and THF (or H) were analysed. In one experiment propene was distilled at 163 K and measured volumetrically.

Analyses.—G.l.c. analysis was carried out using a F + M thermal conductivity instrument equipped with a disc integrator employing a column of Chromosorb WAW coated with 30% (by weight) Carbowax 20M. Both liquid and gas injection were used on this system. In addition, an instrument employing flame ionization detection equipped with an automatic integrator was used in the analysis of six experiments. In this case a 2·3 m × 2 mm glass column packed with Chromosorb 103 was used. At 130° the retention times observed (disc integrator) (in min) were: propene, 1·3; heptane, 3·1; acrolein, 5·3; DAE, 7·1. The response factors relative to heptane were: propylene, 1·433; acrolein, 1·636; and DAE, 1·176. For the automatic integrator system the retention times were: THF 5·8 and DAE 7·7. All analyses were carried out at least in duplicate and were reproducible within 1%. Agreement between analyses carried out on the thermal conductivity and flame ionization detection instruments was within 5%. Products were identified by comparing the g.l.c. retention times with those of known samples.

RESULTS

The gas-phase thermal decomposition of DAE was studied in the temperature range 545—627 K. All experiments were carried out using DAE and an internal standard except for two in which an excess of toluene or hexene were added as diluent. The only products observed were propene and acrolein.

As indicated by the results in the Table, propene and acrolein were formed in essentially equimolar amounts regardless of temperature, pressure, conversion, or surface : volume ratio of the reaction vessel. Estimation of propene and acrolein was only carried out for those experiments analysed by gas injection of the total reaction mixture. Conversions were measured using the internal standard technique. The results presented in the Table demonstrate good agreement in conversions throughout,



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‡ Throughout this paper, 1 Torr = (101·325/760) kN m^{-2} and 1 cal = 4·184 J.

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always within 10% and for the most part within 5%. In one experiment in which propene was distilled from the reaction mixture and measured volumetrically, good agreement with the internal standard method was also obtained.

First-order rate constants were calculated based on THF or H as internal standard. The reliability of this method is demonstrated by the agreement obtained using two starting mixtures and two independent analytical instruments. The kinetic data are summarized in the Table. Consistent rate constants were obtained despite a 13-fold pressure variation (at 568 K) and the presence of a 5·8-fold excess of toluene or hex-1-ene. The rate constants were also found to be independent of the extent of conversion over a range of 8—73% overall and 20—73% at one temperature (604 K). The reaction appears to be homogeneous since rate constants obtained in a packed vessel of 15-fold greater surface : volume ratio are in good agreement with those obtained from the unpacked vessel.

Kinetic data of the unimolecular decomposition of DAE in the gas phase

T/K	p(DAE)$_0$/ Torr [a]	t/min	Conversion (%) G.l.c.	Propene	Acrolein	10^4k_1/ s^{-1}
549·6	11·4	60	12·3	12·0	14·2	0·3640
548·1	9·6	40	8·0	13·6	13·1	0·3455
547·3	14·8	69	10·7	11·8	14·1	0·2729
546·4	10·7	95	13·7	15·4	13·2	0·2597
546·0	4·7	85	13·3	14·7	10·4	0·2801
544·9	5·5	150	20·7	22·0	21·1	0·2574
545·1	5·7	120	18·1	19·0	18·1	0·2779
543·9	69·1	65	10·3			0·2784
561·4	26·7 P	75	32·6	34·4	33·3	0·8776
561·6	25·3 P	120	44·8	45·1	44·0	0·8263
567·3	11·4	50	30·7	31·5	32·6	1·223
568·6	6·6	75	53·7	45·8	43·9	1·384
568·6	12·4	90	52·0	53·0	52·9	1·358
568·0	83·5	30	32·4			2·174
568·0	17·7	65	35·7			1·134
568·2	33·5	97	49·5			1·172
568·3	85·7	45	31·1			1·337
569·4	48·9	70	30·4			1·210
585·1	8·9	30	46·7	47·9	47·7	3·499
584·5	12·5	45	59·4	62·9	62·1	3·337
584·8	7·8	15	27·5	27·8	28·2	3·569
584·6	14·7	25	42·5	44·0	43·6	3·688
587·1	77·5	20	37·3			3·888
603·7	10·4	5	27·6	28·4	28·8	10·74
604·5	5·9	10	52	44·9	54·2	12·24
604·6	11·2	4	19·5	24·4	26·4	9·05
605·7	11·0	20	73·3	77·4	88·3	11·02
604·5	25·9	5	27·0	27·5		10·47
604·4	24·1	11	49·3			10·28
604·5	11·2	10	37·7			7·87
604·9	21·1 [b]	6·5	33·3			10·37
622·3	17·7	4	54·3			32·64
622·1	16·6	2·5	37·1	40·5	37·1	31·80
625·6	15·3	3	48·8	50·0	48·4	37·17
627·3	18·3	5	69·2		75·9	39·20
627·2	11·6	3	51·4		54·5	40·49
627·2	17·7	3·5	56·1	62·6	62·5	39·25
627·4	19·7 [c]	4	62·2			40·49
616·5	44·4 P	4	38·1	41·5	38·2	19·99
618·6	36·7 P	3	38·4	45·3	40·3	26·91
624·7	46·7 P	3	45·4	49·8	49·1	33·58
625·2	11·9 P	5	63·2	63·1	61·3	33·33

[a] Starting pressure. P indicate experiments carried out in a packed vessel. [b] Carried out in a 5·8-fold excess of toluene. [c] Carried out in a 5·8-fold excess of hex-1-ene.

A linear least squares analysis of the data, including the points obtained using the packed vessel, yields the Arrhenius relationship (1) where the errors given are standard deviations.

$$\log (k_1/\mathrm{s}^{-1}) = 11\cdot83 \pm 0\cdot13 - (40\cdot90 \pm 0\cdot35\ \mathrm{kcal\ mol}^{-1})/2\cdot3RT \quad (1)$$

From known thermodynamic data[10] and applying the method of group additivities,[11] the equilibrium constant for the reaction of DAE to give propene and acrolein is calculated to be $\log (K/\mathrm{atm}) = 2\cdot9 + (14\cdot64\ \mathrm{kcal\ mol}^{-1})/2\cdot3RT$. Hence the reaction is thermodynamically irreversible.

DISCUSSION

The thermal decomposition of diallyl ether is a clean, homogeneous reaction, obeying first-order kinetics. On the basis of the stoicheiometric formation of propene and acrolein and the agreement in conversions based on depletion of the starting material and formation of products, the reaction appears to be unimolecular.

The observed A factor of $10^{11\cdot8}$ s^{-1}, corresponding to a net loss in entropy of 8·0 cal mol^{-1} K^{-1} in the transition state, is consistent with the assumption of a six-centre transition state. Using the method of O'Neal and Benson[12] a value of $10^{11\cdot3}$ s^{-1} is predicted. The observed Arrhenius parameters are in line with those found for the analogous concerted retro-'ene' elimination reactions of *N*-alkyl-*N*-allylamines,[1-4] hepta-1,6-diene,[6] butenoic acids,[7] but-3-enols,[8] and allyl methyl ether.[9]

From the results presented here, a vinyl substituent bonded to the carbon atom carrying the hydrogen atom which undergoes a shift, reduces the activation energy by 2·7 kcal mol^{-1} for the ethers, compared to the 5·2 kcal mol^{-1} for the corresponding amines.[1] In contrast, homopolar, concerted, six-centre reactions generally exhibit only very weak substituent effects.

The observed decrease in activation energy can readily be rationalized by a polarizability stabilization concept,[13] since vinyl substituents are known to stabilize adjacent positive sites at least as well as radical sites.[14,15] The finding that the stabilizing effect of vinyl (on the carbon atom from which hydrogen is removed) is smaller in ethers than in amines by an amount clearly outside experimental error, would imply considerably less polarization in the transition state of allyl ethers as opposed to allylamines.

Our findings on the substituent effects in allyl ether decomposition are in agreement with those of Cookson and Wallis,[16] who, on the basis of relative rate studies, favoured a transition state with only small charge separation.

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