1331. *Pyrolysis Studies. Part XVI.*[1] *A Mechanistic Study of the Pyrolysis of β-Hydroxy-olefins*

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The pyrolysis of β-hydroxy-olefins to olefins and carbonyl compounds has been shown to be a first-order homogeneous unimolecular reaction. Alkyl groups at the 1-position of but-3-en-1-ol have much less effect on the rate of pyrolysis than when they are in a structurally similar position of ethyl formate. This implies that there is less heterolytic splitting of the C–CHOH bond in β-hyroxy-olefins in the transition state than C–O splitting in ester pyrolysis. A 3-phenyl substituent in but-3-en-1-ol increases the rate of pyrolysis more than similar substitution in ethyl formate. Apparently there is greater use of the π-electrons in the transition-state pyrolysis of β-hydroxyolefins than in ester pyrolysis.

Tertiary alcohols decompose more readily than secondary and primary alcohols. A comparison of the entropies of activation indicates that tertiary alcohols are in a more favourable conformation for thermal decomposition than the primary alcohols.

β-HYDROXY-OLEFINS are known [2] to pyrolyse in the gas phase to olefins and the aldehyde or ketone according to the equation

$$R\cdot CH{:}CH\cdot CH_2\cdot CR'_2\cdot OH \longrightarrow R\cdot CH_2\cdot CH{:}CH_2 + R'_2CO$$

From a study of the products of pyrolysis of 3-ethyl-6-phenyl-hex-5-en-3-[^{2}H]ol, Arnold and Smolinsky [3] proposed a six-membered ring for the transition state.

$$PhCH{:}CH\cdot CH_2\cdot C(Et)\cdot CH_2\cdot CH_2\cdot OD \longrightarrow PhCHD\cdot CH{:}CH_2 + Et_2CO$$

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[1] Part XV, *J. Org. Chem.*, 1965, **30**, 434.

[2] C. D. Hurd, " The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, p. 164.

[3] R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, 1959, **81**, 6443; *J. Org. Chem.*, 1960, **25**, 129.

Smith and Taylor[4] supported this by showing that the pyrolysis was strictly first-order, and that it had a small negative entropy of activation (—4·9 e.u. at 600°K). This cyclic transition state would structurally resemble those suggested for the pyrolsyis of carboxylic esters[5] and βγ-unsaturated acids.[6]

This Paper reports how substituents at the 1-, 3-, and 4-positions of but-3-en-1-ol influence the rate and reaction parameters in the thermal decomposition, and compares these results with effects brought about by similar substitutions in the pyrolysis of esters.

EXPERIMENTAL

Preparation of the β-Hydroxy-olefins.—But-3-en-1-ol and pent-4-en-2-ol were purchased; the other alcohols were prepared as described below. All the alcohols were carefully fractionated before use, and tested for purity by gas chromatography on a 1·5-m. column packed with Dow silicon 710 on firebrick.

2-Methylpent-4-en-2-ol was prepared (38%) by the method of Henze, Allen, and Leslie[7] from allylmagnesium bromide and acetone; b. p. 112—114°/645 mm., n_D^{20} 1·4261 (lit.,[7] b. p. 117°/775 mm., n_D^{20} 1·4263). 4-Phenylbut-3-en-1-ol, m. p. 35—36° (lit.,[8] 36°), was prepared by the reduction of ethyl styrylacetate with lithium aluminium hydride. Styrylacetic acid was prepared (21%) from phenylacetaldehyde and malonic acid,[9] and esterified with ethanol and concentrated sulphuric acid. 3-Phenylbut-3-en-1-ol was prepared (52%) by the condensation of α-methylstyrene with formaldehyde according to the method of Hawkins and Thompson;[10] b. p. 68°/0·1 mm., n_D^{20} 1·5582 (lit.,[10] 130—131°/13 mm., 1·5581). But-3-en-1-ol had b. p. 110°/640 mm., n_D^{20} 1·4221 (lit.,[11] 112—113°/748 mm., 1·4224), and pent-4-en-2-ol, b. p. 112°/640 mm., n_D^{20} 1·4241 (lit.,[12] 115°/775, 1·4240).

Method of Pyrolysis.—All the β-hydroxy-olefins were pyrolysed at temperatures ranging from 332·5 to 426·9° in a stainless steel static reactor of constant volume (200 ml.) whose design and operation have been described.[13] The reaction was followed by automatically measuring the increase in pressure inside the reactor by the use of a stainless steel diaphragm (closing one end of the reactor) as a null-point gauge and a pressure transduce rconnected to a strip-chart recorder. The temperature was maintained to within 0·02° with a large electrically heated aluminium block lagged with glass wool. The temperature was calibrated with a platinum resistance thermometer. The surface of the reactor was carefully deactivated by leaving the products from the pyrolysis of but-3-enoic acid at 400° for several days in the reactor, and by pyrolysing the compound under study until reproducible results were obtained. The homogeneity of the reaction was evaluated by establishing that it was first-order, and that the rate was not changed by a ten-fold change in the surface-to-volume ratio. The addition of cyclohexene did not alter the rate beyond experimental error. The rates of pyrolysis of standards (t-butyl acetates and 1-phenylethyl carbonate) were periodically determined, to evaluate further if any wall-reaction was occurring. Precautions were taken to exclude air from the reactor since air reactivates the surface.

The liquid alcohols were injected undiluted, and 4-phenylbut-3-en-1-ol and 3-phenylbut-3-en-1-ol were introduced both as melts (using a heated syringe) and as solutions (in chlorobenzene). Chlorobenzene is an inert, stable solvent and was shown not to influence the rate of pyrolysis.

After the conditions of the reactor had been carefully standardised all the rate constants were determined at least in triplicate. The reactions were first-order over 90% of their course, and P_∞ was twice P_0.

Product Analysis.—To be certain of the reaction under study, the products were characterised by gas chromatography (Dow silicone 710 and silica gel column). For example, the products trapped from the pyrolysis of but-3-en-1-ol (Ia) were shown to be propene and formaldehyde.

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[4] G. G. Smith and R. Taylor, *Chem. and Ind.*, 1961, 949.
[5] C. H. DePuy and R. W. King, *Chem. Rev.*, 1960, **60**, 431.
[6] G. G. Smith and S. E. Blau, *J. Phys. Chem.*, 1964, **68**, 1231.
[7] H. R. Henze, B. R. Allen, and W. B. Leslie, *J. Org. Chem.*, 1942, **7**, 328.
[8] H. Normant, *Compt. rend.*, 1948, **226**, 732.
[9] R. P. Linstead and L. T. D. Williams, *J.*, 1926, 2735.
[10] E. G. C. Hawkins and R. D. Thompson, *J.*, 1961, 370.
[11] A. Juvala, *Ber.*, 1930, **63**, 1992.
[12] J. Baudrengheim, *Bull. Soc. chim. belges*, 1923, **32**, 338.
[13] G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, 1963, **28**, 3496.

Pent-4-en-2-ol (IIa) produced propene and acetaldehyde. No other products were obtained. These results, plus the facts that $P_\infty = 2P_0$, and that the kinetics could be followed to greater than 90%, establish the stoicheiometry of the reaction.

RESULTS

The rates of pyrolysis of the β-hydroxy-olefins are given in Table 1. For all the alcohols, plots of $\log_{10} (P_\infty - P_t)$ against time were linear up to at least 90% decomposition, giving reproducibility of ±2% in the rate constants. Also, in every case the rate constants were independent (±2%) of a four-fold variation in the initial pressure and a similar excess of added nitrogen, and the final pressure was twice the initial pressure. This confirms the earlier report [4] of first-order kinetics.

The Arrhenius plots were linear for all the compounds studied, and derived energies and entropies of activation at 650°K are given in Table 1; they are estimated to be accurate to within ±1·5 e.u. Also in Table 2 are the calculated rates of reaction at 650°K.

The reaction was homogeneous, since the insertion into the reactor of a stainless steel sponge (Gottschalk No. 725), which increased the surface area ten times, did not alter the rate. For example, after complete deactivation of the new surface a rate constant of $9{\cdot}20 \times 10^{-3}$ sec.$^{-1}$ at 655·2°K was obtained for the pyrolysis of pent-4-en-2-ol, and $10{\cdot}2 \times 10^{-3}$ sec.$^{-1}$ at 636·6°K for 3-phenylbut-3-en-1-ol. The rate constants for these reactions in the unpacked reactor were, respectively, $9{\cdot}31 \times 10^{-3}$ sec.$^{-1}$ (655·2°K) and $9{\cdot}89 \times 10^{-3}$ sec.$^{-1}$ (631·0°K).

TABLE 1

Rates of pyrolysis and reaction parameters for β-hydroxy-olefins

Compound	Temp. (°C)	10^3k (sec.$^{-1}$)	10^3k at 650° (sec.$^{-1}$)	Arrhenius energy (kcal.)	$\Delta S^\ddagger$ e.u. at 650°
But-3-en-1-ol (Ia)	370·2	1·78			
	380·8	3·04	2·51	41·0	−8·8
	400·0	7·31			
	412·0	12·6			
Pent-4-en-2-ol (IIa)	351·9	2·06			
	365·1	4·06	7·37	40·9	−7·5
	382·0	9·31 *			
	389·6	13·2			
2-Methylpent-4-en-2-ol (IIIa)	334·2	1·41			
	346·4	2·72	13·6	40·7	−6·3
	358·3	4·99			
	370·0	9·18			
3-Phenylbut-3-en-1-ol (IVa)	332·1	1·55			
	334·5	3·05	24·7	38·9	−7·8
	346·4	5·58			
	357·8	9·89			
4-Phenylbut-3-en-1-ol (V)	388·3	0·950			
	400·0	1·62	0·537	42·8	−9·1
	412·0	2·84			
	426·6	5·09			
3-Ethyl-6-phenylhex-5-en-3-ol (VI)†	377·9		9·50	41·8	−5·3

* This alcohol when dissolved in twice its volume of cyclohexene gave a rate of $9{\cdot}38 \times 10^{-3}$ at 382·0°. † Calculated from the data in ref. 4.

TABLE 2

Comparison of the rates (10^3k, sec.$^{-1}$) of pyrolysis (at 650°K) of structurally similar compounds

β-Hydroxy-olefin			Ester			βγ-Unsat. acid		
$H_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	(Ia)	2·51	$O{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH_3$	(Ib)	0·31	$H_2C{:}CH{\cdot}CH_2{\cdot}CO{\cdot}OH$	(Ic)	13·0
$H_2C{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH$	(IIa)	7·37	$O{:}CH{\cdot}O{\cdot}CHMe{\cdot}CH_3$	(IIb)	5·6	—		
$H_2C{:}CH{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$	(IIIa)	13·6	$O{:}CH{\cdot}O{\cdot}CMe_2{\cdot}CH_3$	(IIIb)	230	—		
$H_2C{:}CPh{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	(IVa)	24·7	$O{:}CPh{\cdot}O{\cdot}CH_2{\cdot}CH_3$	(IVb)	1·97 *	—		
$PhHC{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	(V)	0·537	—			—		
$PhHC{:}CH{\cdot}CH_2{\cdot}CEt_2{\cdot}OH$	(VI)	9·50	—			—		

* At 687·2°K.

Finally, the molecular nature of the reaction was indicated by the introduction of cyclohexene, which, because of its inhibiting effects, would have markedly altered the rate if a radical chain reaction were occurring. The injection of twice the volume of cyclohexene did not affect the rate.

Discussion

The results listed in Tables 1 and 2 indicate that there is a similarity in the pyrolytic reactions of β-hydroxy-olefins, esters, and βγ-unsaturated acids. Based on the products formed, volume-to-surface ratio, and inhibitor studies, it appears that these reactions proceed through a homogeneous non-radical reaction. The Arrhenius activation energies for the thermal decomposition of but-3-en-1-ol (Ia), ethyl formate[14] (Ib), and but-3-enoic acid[6] (Ic) are close together (41·0, 44·1, and 39·3 kcal./mole), and the entropies of activation are nearly the same (−8·7, −8·1, and −8·8 e.u.). From these Arrhenius parameter values, and the fact that the reactions are all homogeneous unimolecular reactions, there is strong support that a cyclic transition-state mechanism is favoured in the pyrolyses.

As the effects on the rate of substitution in the three systems are compared some striking differences are noted.

The Influence of Branching at the Hydroxyl Carbon.—Branching at the C-atom where cleavage occurs has a marked effect upon the rate of pyrolysis, particularly of the esters. The relative rates in the pyrolysis at 650°K of ethyl formate (Ib), isopropyl formate (IIb), and t-butyl formate (IIIb) are 1 : 18 : 760.[15] For the structurally similar β-hydroxy-olefins, but-3-en-1-ol (Ia), pent-4-en-2-ol (IIa), and 2-methylpent-4-en-2-ol (IIIa), the relative rates are 1 : 3 : 5·4 [compare also (V) and (VI)]. The reason why increased branching increases the ease of pyrolysis of the carboxylic esters is probably that heterolytic splitting of the C–O bond is made easier by the increased stabilisation of the partial positive charge formed on the carbon atom of the C–O bond. Apparently, splitting of the C–COH bond is not as fully developed in the transition state of β-hydroxy-olefins as in the breaking of the C–O bond in ester pyrolysis, as branching at this position has little effect on the rate of pyrolysis.

The increase in rate as the branching increases from primary to tertiary alcohols, (Ia), (IIa), (IIIa), may reflect a more rigid conformation of the tertiary alcohol, thus requiring less change in configuration in going from the ground state to the transition state. The crowding of the methyl groups forces the hydroxyl group to lie close to the π-electrons of the double bond, and hence lowers the free-energy of activation; models indicate this crowding. It is noteworthy that, whereas the energies of activation of (Ia), (IIa), and (IIIa) are within experimental error (Table 1), the entropy of activation of the primary alcohol (Ia) is the most negative (−10·5 e.u.) and that of the tertiary alcohol (IIIa) is the least negative (−7·5 e.u.). This could indicate that less change in conformation is required in going from the ground state to transition state in the tertiary alcohol than in the primary alcohol.

Influence of the Acidity of Hydroxyl Hydrogen.—The proposed transition state for the pyrolysis of but-3-en-1-ol (Ia) is structurally similar to that for but-3-enoic acid (Ic) (Table 2). A comparison of the rates of pyrolysis at 650°K of the former compound ($2{\cdot}51 \times 10^{-3}$ sec.$^{-1}$) with that for the latter ($13{\cdot}0 \times 10^{-3}$ sec.$^{-1}$) reveals that, despite the higher acidity of the hydroxyl hydrogen in but-3-enoic acid, this compound is pyrolysed at only five times the rate of but-3-en-1-ol. Also, the rates of pyrolysis of but-3-en-1-ol, pent-4-en-2-ol, and 2-methylpent-4-en-2-ol are in the opposite order to their acidities, although this may not be too significant, since, as stated above, other factors may be operative. It appears, then, that in the pyrolysis of β-hydroxy-olefins and βγ-unsaturated acids the acidity of the hydroxyl hydrogen is not a major factor in determining the rate. Similarly, it has been found that in the pyrolysis of carboxylic esters the acidity of the β-hydrogens of the ester group, which are structurally in a similar position to the hydroxyl

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[14] Calculated from the data of A. T. Blades, *Canad. J. Chem.*, 1954, **32**, 366.

[15] Calculated from the data of E. Gordon, S. J. W. Price, and A. F. Trotman-Dickenson, *J.*, 1957, 2813.

hydrogen of the β-hydroxy-olefins and the βγ-unsaturated acids, has also been shown not to be a major factor in determining the rate of pyrolysis.[16]

Effects of Phenyl Groups Substituted on the Double Bond.—Unlike substitution at the 1-position of but-3-en-1-ol, which has little effect on the rate of pyrolysis in comparison to analogous substitution in carboxylic esters, substitution at the 3-position of but-3-en-1-ol has considerably more influence than is found by a similar substitution with carboxylic esters. Thus, at 650°K, 3-phenyl-but-3-en-1-ol pyrolyses at ten times the rate for but-3-en-1-ol ($24{\cdot}7 \times 10^{-3}$ to $2{\cdot}51 \times 10^{-3}$ sec.$^{-1}$, respectively), while ethyl benzoate (IVb) and ethyl formate (Ib), which are structurally similar (Table 2) to 3-phenyl-but-3-en-1-ol (IVa) and but-3-en-1-ol (Ia), pyrolyse at the same rate ($1{\cdot}95 \times 10^{-3}$ [17] and $1{\cdot}97 \times 10^{-3}$, respectively, at 687·2°K).

A logical explanation for the fact that 3-phenylbut-3-en-1-ol (IVa) reacts fast than but-3-en-1-ol (Ia) is that in the former compound the phenyl group stabilises the partial positive charge which develops in the transition state as the π-electrons of the double bond are used to co-ordinate with the hydroxyl hydrogen. In the ester series the β-hydrogens apparently co-ordinate with an unshared pair of electrons on the oxygen and not the π-system. The charge density, therefore, at the carboxyl carbon is not principally affected in the transition state and hence substitution at this position has little effect.

A phenyl group substituted at the 4-position of but-3-en-1-ol slows the rate of pyrolysis, *e.g.*, but-3-en-1-ol (Ia) pyrolyses almost five times as fast as 4-phenylbut-3-en-1-ol (V), and 2-methylpent-4-en-2-ol (IIIa) pyrolyses 1·65 times faster than 3-ethyl-6-phenylhex-5-en-3-ol (VI) (Table 1). The effect of a phenyl substituent at this position could perhaps be predicted, since, during the course of the reaction, the double bond shifts from the phenyl substituent; the conjugation energy of the double bond in styrene with the ring is estimated to be from 2 to 4 kcal.[18]

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[16] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.

[17] G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, 1963, **28**, 403.

[18] G. N. Wheland "Resonance in Organic Chemistry," Wiley, New York, 1955, p. 102.