Kinetics of the Gas-phase Pyrolysis of 1-t-Butylbut-3-enyl Acetate

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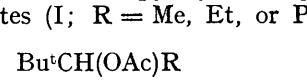
The pyrolysis of 1-t-butylbut-3-enyl acetate has been studied in a static system in the temperature range 300—350 °C and pressure range 35—300 mmHg. The reaction is homogeneous and of the first order. The rate of the reaction is given by the equation log (k_1/s^{-1}) = 14·14 ± 0·01 − (46,400 ± 600) cal mol^{-1}/2·303 RT. The effect of a β-unsaturated substituent in the elimination of secondary acetates is discussed.

THE transition state in ester pyrolysis has generally been accepted as six-centred.[1] However, several results and kinetic analyses have provoked considerable interest and discussion concerning the nature of the mechanism of this reaction.[2-17]

A large number of comparative rates in the pyrolysis of secondary acetates have been measured for alkyl substituents whose inductive (+I) effects apparently do not affect dramatically the proposed six-centred cyclic transition state. Nevertheless, there are a few papers dealing with substituted secondary acetates, in which the electronic spectra of the alkyl group vary markedly, which have indicated that the transition states of these reactions are different from those states which evince a symmetrical distribution of electrons.[11,18-20]

Work [21] on the pyrolysis of highly branched secondary acetates (I; R = Me, Et, or Pr^i) suggested, from the

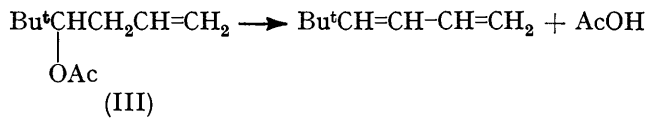


Bu^{t}CH(OAc)R (I) MeCH(OAc)R (II)

relative reactivities, the importance of opposing effects along this series. The nature of these effects has been already elucidated [22] from studies using a flow technique of a series of esters. Since the rate relationships obtained for (I) shows that the +I effect of the alkyl groups does not affect the transition state dramatically, this work aims at examining the relative effect of R in (I) when it is unsaturated. The specific compound studied is 1-t-butylbut-3-enyl acetate (III).

RESULTS AND DISCUSSION

The products of decomposition of ester (III), in a vessel seasoned with allyl bromide, are mainly *trans*-5,5-dimethylhexa-1,3-diene, a small amount of *cis*-5,5-dimethylhexa-1,3-diene, and acetic acid. The stoicheiometry based on (III) implies that for long reaction times



Bu^{t}CH(OAc)CH$_2$CH=CH$_2$ ⟶ Bu^{t}CH=CH−CH=CH$_2$ + AcOH (III)

the final pressure P_f should be twice the initial pressure P_0. Experimentally, it was found from an average of four runs that P_f/P_0 = 1·96. Moreover, the stoicheiometry of this reaction has also been verified, within the limits of analytical error, by the agreement of the percentage decomposition determined from pressure measurements with that determined by chromatography.

The reaction is homogeneous in a clean or seasoned vessel. An increase in the surface : volume ratio of 4 and 6·8 relative to the normal vessel had no significant effect on the rate constants for the decomposition.

The analyses of the products of decomposition of acetate (III) in an unpacked, clean, Pyrex vessel are given in Table 1. The absence of a free radical reaction

TABLE 1

Product analysis for decomposition of ester (III)

Temp. (°C)	Reaction time (min)	% *trans*	% *cis*	*trans* : *cis*
296·3	35	94·7	5·3	17·9
316·2	37	94·9	5·1	18·4
319·1	34	94·8	5·2	18·2

was demonstrated by carrying out several runs in the presence of cyclohexene. The presence or absence of the inhibitor gives no significant change in the mean value of the reaction velocities (Table 2).

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The rate constants of pyrolysis are independent of the initial pressure of the ester (Table 3) and first-order plots are linear up to 60% decomposition. The temperature dependence of the reaction velocities is shown in Table 4.

TABLE 2

Effect of cyclohexene inhibitor on rates at 316·2 °C

P_e/mmHg	P_c/mmHg	P_e/P_c	$10^4k/s^{-1}$
178·2	0·0		9·00
85·9	42·7	2·04	9·06
81·5	80·3	1·02	9·15
121·2	234·0	0·52	9·10

P_e and P_c are the initial pressures of the ester and the cyclohexene respectively.

TABLE 3

Variation of rate constants with initial pressure at 306·7 °C

P_0/mmHg	41	80	93	104	160	174	198
$10^4k/s^{-1}$	4·29	4·41	4·55	4·56	4·61	4·64	4·78

TABLE 4

Variation of rate constants with temperature

Temp. (°C)	300·2	306·7	316·2	319·1	325·8	334·2	341·3	349·1
No. of runs	9	12	8	9	11	8	10	7
$10^4k/s^{-1}$	2·85	4·54	9·00	10·90	17·21	28·87	44·35	69·25

From the experimental results, the Arrhenius equation obtained by means of least-square procedure is $\log (k_1/s^{-1}) = 14{\cdot}14 \pm 0{\cdot}01 - (46{,}400 \pm 600)$ cal mol^{-1}/ $2{\cdot}303RT$. The errors were calculated with a confidence coefficient of 0·8 in order to give more reliable values for the limits. The Arrhenius parameters for a related series of esters are shown in Table 5. The effect of the β-methyl substituents (Table 5) is not easily explained and may be indicative of a six-centred cyclic transition state. However, a substituent of different u.v. spectral properties such as a vinyl group gives a significant increase in the rate of elimination suggesting that such decomposition may well involve a discreet charge separation in the transition state.

To provide additional evidence for this observation, secondary acetates of type (II) (Table 6) were compared by dividing the overall rate constant into partial rates for the methyl group k_{Me} and for the alkyl group $k_{CHR^1R^2}$ with the aid of the product distribution of olefins reported in the literature.[18,23] Further, the partial rates per β-hydrogen $k^H{}_{Me}$, $k^H{}_{CHR^1R^2}$ were calculated and show to be almost constant, except for $k^H{}_{CHR^1R^2}$ of 1-methylprop-2-enyl acetate. Again, the vinyl substituent clearly has a marked effect on the acidity of the β-hydrogen atoms in increasing the rate and in forming an oxygen–hydrogen bond in the transition state. Similarly, a β-substituent such as the acetyl group, which has a $-I$ effect, also has a considerable influence.[18]

EXPERIMENTAL

In order to prepare the acetate (III), neopentyl alcohol was oxidized to pivaldehyde,[24] which when treated with the Grignard reagent of allyl bromide [25] gave 2,2-dimethylhex-5-en-3-ol (69%), b.p. 119—121° at 633 mmHg. The alcohol was then acetylated in the usual manner [26] (57%), b.p. 125—127° at 634 mmHg. The ester was fractionated several times and the fraction of 99·1% purity (g.l.c.) was used. 5,5-Dimethylhex-1,3-diene was prepared as previously described.[27] The olefin and starting reagent were determined quantitatively (using internal standards) on a Perkin-Elmer F11 gas chromatograph with a flame ioniz-

TABLE 5

Kinetic parameters for pyrolysis of $Bu^tCH(OAc)CHR^1R^2$ at 330 °C

R^1	R^2	$10^4k_1/s^{-1}$	Rate per β-hydrogen	Relative rate per β-hydrogen	E_a/cal mol^{-1}	log (A/s^{-1})	Ref.
H	H	3·81	1·27	1·00	44,200 (±900)	12·58 (±0·01)	21
H	Me	6·61	3·31	2·61	44,800 (±400)	13·04 (±0·01)	21
Me	Me	1·78	1·78	1·40	46,300 (±300)	13·03 (±0·01)	21
H	$CH{=}CH_2$	21·9	10·95	8·62	46,400 (±600)	14·14 (±0·01)	This work

TABLE 6

Kinetic parameters for pyrolysis of $MeCH(OAc)CHR^1R^2$ at 360 °C [a]

R^1	R^2	$10^4k_1/s^{-1}$	Rate per β-hydrogen	E_a/cal mol^{-1}	log (A/s^{-1})	10^4k_{Me}	$10^4k_{CHR^1R^2}$	$10^4k^H{}_{Me}$	$10^4k^H{}_{CHR^1R^2}$	Ref.
H	H	27·7	4·62	47,500 (±1,900)	13·85 (±0·01)	13·9	13·9	4·6	4·6	23
H	Me	25·9	5·18	47,200 (±1,300)	13·70 (±0·01)	14·8	11·1	4·9	5·6	23
Me	Me	24·9	6·23	45,600 (±500)	13·13 (±0·01)	17·6	5·0	5·9	5·0	23
H	$CH{=}CH_2$	46·8	9·36	44,600 (±600)	13·05 (±0·01)	16·4	30·4	5·5	15·2	18

[a] The Arrhenius parameters were recalculated from the rate–temperature data by the least-square procedure. The confidence coefficient in parentheses used to determine the errors was 0·8.

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ation detector. A bis-2-methoxyethyl adipate on 5% Chromosorb G.A.W. D.M.C.S. 80—100 mesh column was used for the olefin and ester analyses. The purity of the starting material and products was additionally verified with a Hitachi–Perkin-Elmer RMU-6H mass spectrometer, and by i.r. and n.m.r. spectroscopy. The least-squares calculations were performed with an IBM 1130 computer.

Measurements of rates were performed in a static system in vessels seasoned by the products of decomposition of allyl bromide,[28,29] the reaction being followed manometrically.

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