The Gas-phase Pyrolysis of 1,2-Dimethylpropyl Acetate

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The pyrolysis of 1,2-dimethylpropyl acetate has been studied in a static system in the temperature range 310—370° and pressure range 30—300 mmHg. The reaction is homogeneous, follows a first-order rate law, and is unimolecular, the rate constant being given by $\log [k_1\ (\mathrm{s}^{-1})] = 13{\cdot}123 \pm 0{\cdot}006 - (45{,}570 \pm 480)/2{\cdot}303RT$. The role of β-alkyl groups in eliminations from secondary acetates is discussed.

ACETATES of aliphatic alcohols with β-C–H bonds normally decompose by a *cis*-elimination to yield olefins and acetic acid. The mechanism of these reactions is widely accepted as involving a six-centred transition state.[1] The object of the present work is to complete the study of the effect of β-methylation on the rate of pyrolysis of secondary acetates of structure MeCH(OAc)R where R = H, Me, Et, $\mathrm{Pr^i}$, and $\mathrm{Bu^t}$. The pyrolyses of ethyl,[2] isopropyl,[3-5] s-butyl,[4] and pinacolyl acetates[6] have all been reported, but 1,2-dimethylpropyl acetate has not been previously studied. This latter compound has now been investigated, thus enabling the effect upon the rate constant of the methyl group to be determined.

RESULTS AND DISCUSSION

The products of decomposition of 1,2-dimethylpropyl acetate, in a vessel seasoned with allyl bromide are predominantly 3-methylbut-1-ene, a smaller amount of the isomer 2-methylbut-2-ene, and acetic acid. The stoicheiometry based on equation (1) would lead to a

$$\mathrm{Me_2CH{\cdot}CH(OAc)Me} \longrightarrow \mathrm{C_5H_{10}} + \mathrm{HOAc} \qquad (1)$$

ratio of 2 for $P_f : P_0$, where P_f and P_0 are the final and initial pressures respectively. Six measurements in the temperature range 320—370° with initial pressures around 180 mmHg gave a mean value of 1·98. The stoicheiometry was further confirmed by a comparison (Table 1) of the percentage decomposition determined from pressure with that determined by chromatography.

TABLE 1

The stoicheiometry of the reaction

Time (min)	2·5	8·5	20	30	60
Decomp. (%) (press.)	18·3	51·0	80·8	91·5	89·4
Decomp. (%) (chrom.)	18·7	50·4	81·8	90·5	98·9

The reaction is homogeneous in a clean or seasoned Pyrex vessel. An increase in the surface : volume ratio by factors of 4·0 and 6·8 relative to the unpacked vessel had little effect on the rate specially in the seasoned vessel (Table 2).

Although there appears to be a slight increase in rate in a clean vessel of S/V 6·8, the olefin product composition is almost identical with that obtained in a seasoned vessel. In seasoned vessels, the olefins composition is almost independent of temperature (Table 3), all analyses being done after reaction for 30 min. The pure olefins A and B do not isomerise in a seasoned vessel over a period of 1 h at 350°.

TABLE 2

The homogeneity of the reaction (329·8°)

S/V (cm^{-1})	No. of runs	10^4k (s^{-1}) *	No. of runs	10^4k (s^{-1}) †
1	12	4·02	7	4·12
4	8	4·02	7	4·12
6·8	5	3·96	5	4·46

* Allyl bromide seasoned. † Clean Pyrex.

TABLE 3

Distribution of olefins from pyrolysis of 1,2-dimethylpropyl acetate. Vessel S/V = 1 and seasoned with allyl bromide

Temp. (°C)	Reaction/ %	A (%) *	B (%) †	A/B
319·8	32·2	24·2	6·08	3·98
329·7	52·0	38·8	10·5	3·70
349·8	91·5	70·5	20·0	3·53

* A = 3-methylbut-1-ene. † B = 2-methylbut-2-ene.

The absence of a free radical component of the reaction is indicated by the lack of effect of added inhibitor, cyclohexene or propene (Table 4). Air, and in particular oxygen, were found markedly to accelerate the pyrolysis.

TABLE 4

The effect of added inhibitors

P_0(mmHg)	P_i(mmHg)	P_0/P_i	10^4k_1 (s^{-1})
Inhibitor cyclohexene; temp. 349·8°			
266·5			13·8
75·7	152·5	0·50	13·8
140·2	140·5	1·00	14·0
151·0	74·7	2·02	13·7
Inhibitor propene; Temp. 329·8°			
231·7			4·10
85·7	168·5	0·51	4·12
136·2	133·3	1·02	4·11
171·5	75·9	2·26	4·04

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The rate constants of decomposition were independent of initial pressure of the ester (Table 5) and the first-order plots are linear up to at least 60% decomposition.

TABLE 5

Variation of the rate constants with initial pressure (320°)

P_0(mmHg)	81·6	100·9	145·0	180·7	243·0	271·4	303·5
10^4k_1 (s^{-1})	2·31	2·32	2·28	2·29	2·30	2·20	2·20

The variation of the rate constants with temperature is shown in Table 6. The data in Table 6 were fitted to the

TABLE 6

The temperature dependence of the rate constants

Temp. (°C)	309·9	319·9	329·8	339·8	349·8	359·8	369·8
No. of runs	7	15	12	13	14	14	13
10^4k_1 (s^{-1})	1·07	2·20	4·02	7·63	13·81	24·1	42·8

Arrhenius equation $\log [k_1 (s^{-1})] = 13{\cdot}123 \pm 0{\cdot}006 - (45{,}570 \pm 475)/2{\cdot}303RT$ (R in cal mol^{-1} K^{-1}), the 80% confidence limits being quoted. Arrhenius parameters for a related series of molecules are shown in Table 7.

TABLE 7

The Arrhenius parameters for RCH(OAc)Me elimination at 360°

R	10^4k_1 (s^{-1})	Relative rate per β-hydrogen	E(kcal mol^{-1})	$\log A/s^{-1}$	Ref.
H	1·03	1·00	47·7	12·48	2
Me	27·7	13·5	47·5	13·85	2
Et	25·9	15·1	47·2	13·70	3
Pr^i	24·9	18·2	45·6	13·12	This work
Bu^t	21·6	20·9	44·2	12·58	6

The effect of β-methyl substitution, although small, is significant. This is seen by a comparison of the rate per β-hydrogen atom, which increases continuously down the series.

In order to delineate further the effect of β-methyl substitution, the overall rate constant can be divided into partial rate due to the methyl group k_{Me} and due to the alkyl group k_R with the aid of published olefin compositions.[4,6] Further, the partial rates per β-hydrogen k_{Me}^H and k_R^H can be calculated (Table 8).

TABLE 8

Relative rates of elimination of RCH(OAc)Me at 360°

R	10^4k_R (s^{-1})	10^4k_{Me} (s^{-1})	$10^4k_R^H$ (s^{-1})	$10^4k_{Me}^H$ (s^{-1})
H		1·0		0·3
Me	13·9	13·9	4·6	4·6
Et	11·1	14·8	5·6	4·9
Pr^i	5·0	17·6	5·0	5·9
Bu^t		17·7		5·9

Leaving aside the ethyl compound, the partial rate factors per β-hydrogen atom are almost constant. This rate sequence cannot be correlated with that reported for the alkaline hydrolysis of acetates[8] or with the solvolytic rate constants of the corresponding halides.[9]

EXPERIMENTAL

3-Methylbutan-2-ol and its corresponding acetate were prepared as previously described.[10,11] The ester was fractionated several times and the fraction of 99·88% purity (g.l.c.), n_D^{20} 1·4024, was used. The olefins and the starting reagent were determined quantitatively by the method of internal standards in a Perkin-Elmer F-11 gas chromatograph provided with flame-ionization detector. Di-isodecyl phthalate 5%–Chromosorb G acid washed dimethylchlorosilane 60—80 mesh, 6 ft × 1/8 in, was used as a column for the acetate and olefins. The analyses of the products were done by mass, i.r., and n.m.r. spectrometry. The least square calculations were performed by an IBM 1130 computer.

The ester was pyrolysed in vessels seasoned by the products of decomposition of allyl bromide[12,13] in a static system and the kinetics were followed manometrically.

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