56. *Gas-phase Eliminations. Part III.* The Pyrolysis of Some Secondary and Tertiary Alkyl Acetates.*

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The kinetics of the pyrolysis of isopropyl, s-butyl, t-butyl, and t-pentyl acetate in seasoned vessels have been studied, in order to determine the effect of β-methylation on the rate of pyrolysis. The reactions are all homogeneous and all follow first-order laws. The directions of elimination from s-butyl and t-pentyl acetate under kinetically controlled conditions have been determined by vapour-phase chromatography and confirm the results of earlier qualitative investigations.

The study of the effect of α- and β-methylation on the rate of elimination of olefins from alkyl halides has been useful in assigning a mechanism to this class of reaction.[1] Results already reported (see Table 1 for references) show that for alkyl formates and acetates α-methylation results in an increase in rate. The factor per methyl group is, however,

Table 1.

Relative rates of pyrolysis of esters and halides.†

	Et	Pr^i	Bu^t		Et	Pr^i	Bu^t
Formate (307°)	1[2]	20[2]	2360[3]	Chloride (361°)	1[5]	223[6]	41,000[7]
Acetate (305°)	1[2]	36[2]	3900[4]	Bromide (320°)	1[8]	280[9]	78,000[10]

† The temperature has been chosen so that the isopropyl compound has a rate constant of 10^{-4} sec.$^{-1}$. Superscripts are references.

significantly less than for the halides. It is, nevertheless, significant that for the esters the increase in rate from isopropyl to t-butyl is greater than from ethyl to isopropyl. This suggests that replacement of one α-hydrogen atom by a methyl group increases the effect of subsequent α-methyl-substitution. It is of interest to investigate the effect of β-methylation, and to this end pyrolyses of s-butyl and t-pentyl acetate have been studied. For alkyl halides, the effect of β-methylation is small, introduction of each β-methyl group about doubling the rate. For esters it was expected that the effect would be smaller still, and so in order to get accurate relative rates it was thought desirable to measure the rates of decomposition of isopropyl and t-butyl acetate, as well as those of the s-butyl and t-pentyl compounds.

Both s-butyl and t-pentyl acetate can in principle give, on elimination, mixtures of isomeric olefins, and so vapour-phase chromatography was used to determine the composition of the products. Earlier work in this field [11] has been concerned with establishing the product composition in ester pyrolysis from the viewpoint of preparative organic chemistry. For instance, Bailey and King [12] claimed that secondary and tertiary esters show a high degree of specificity in elimination, the product being the least highly alkylated

* Part I, *J.*, 1958, 2398; Part II, 1961, 2756.

[1] Maccoll, "Theoretical Organic Chemistry," Butterworths Scientific Publns., London, 1959, p. 230.
[2] Blades, *Canad. J. Chem.*, 1943, **32**, 366.
[3] Gordon, Price, and Trotman-Dickenson, *J.*, 1957, 2813.
[4] Rudy and Fugassi, *J. Phys. Chem.*, 1948, **52**, 357.
[5] Barton and Howlett, *J.*, 1949, 165.
[6] Barton and Head, *Trans. Faraday Soc.*, 1950, **46**, 114.
[7] Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.
[8] Thomas, *J.*, 1959, 1192.
[9] Thomas and Maccoll, *J.*, 1955, 979.
[10] Harden and Maccoll, *J.*, 1955, 2454.
[11] DePuy and King, *Chem. Rev.*, 1960, **60**, 431.
[12] Bailey and King, *J. Amer. Chem. Soc.*, 1955, **77**, 75.

ethylene; that is, Hofmann's rule [13] is predominantly obeyed. Froemsdorf *et al.*[14] have, however, shown that while this is true for simple primary acetates it is not entirely true for the secondary and tertiary compounds. Some of their results are shown in Table 2.

TABLE 2.

Olefin compositions (%) from the pyrolyses of some acetates (Froemsdorf *et al.*[14]).

Acetate	Temp.	Alk-1-ene	Alk-2-ene	Acetate	Temp.	Alk-1-ene	Alk-2-ene
Bu^n	500°	100	0	Bu^s	450°	57	43
$CHMe_2{\cdot}CH_2{\cdot}CH_2$...	500	100	0	CMe_2Et	400	76	24

These authors further suggested that the olefin product composition is essentially determined by statistical factors, the product composition being far from the equilibrium composition.

In order to gain a deeper insight into the nature of olefin elimination from esters, the present investigation combines a study of the olefin composition under kinetically controlled conditions with an investigation of the kinetics of the reactions, designed to identify unambiguously the mechanism.

RESULTS

Kinetics of Pyrolysis of Isopropyl and t-Butyl Acetate.—Although studies of both these compounds have been reported,[2,15] a re-investigation was undertaken to compare their behaviour with that of s-butyl and t-pentyl acetate under comparable conditions. Blades,[2] using the toluene flow technique,[16] established that elimination from isopropyl acetate has a homogeneous, unimolecular mechanism in the temperature range 440—530°. The Arrhenius equation reported was $k_1 = 10^{13} \exp(-45{,}000/\boldsymbol{R}T)$ (sec.$^{-1}$). Rudy and Fugassi [4] reported

TABLE 3.

The first-order character of elimination from acetates.

Isopropyl acetate at 346°.					
p_0 (mm.)	152	152	160	172	189
10^4k_1 (sec.$^{-1}$)	33·6	33·6	33·6	33·2	33·8
$t_{\frac{1}{4}}/t_{\frac{3}{4}}$	2·41	2·33	2·41	2·41	2·38
t-Butyl acetate at 279°.					
p_0 (mm.)	135	146	147	172	
10^4k_1 (sec.$^{-1}$)	20·2	20·2	20·6	21·0	
$t_{\frac{1}{4}}/t_{\frac{3}{4}}$	2·40	2·40	2·41	2·43	

TABLE 4.

Variation of the rate constants with temperature.

Isopropyl acetate.					
Temp.	362·2°	354·9°	341·9°	330·1°	313·8°
No. of runs	5	6	6	6	5
10^4k_1 (sec.$^{-1}$)	33·6	19·5	8·61	4·14	1·46
t-Butyl acetate.					
Temp.	290·8°	278·6°	267·2°	255·6°	241·1°
No. of runs	7	4	4	4	5
10^4k_1 (sec.$^{-1}$)	42·6	20·5	9·27	4·08	1·36

$k_1 = 2{\cdot}2 \times 10^{13} \exp(-40{,}500/\boldsymbol{R}T)$ (sec.$^{-1}$) for similar elimination from t-butyl acetate. It was thus considered unnecessary to verify the stoicheiometry, homogeneity, or unimolecular nature of these decompositions. However, for both compounds, the ratio $t_{\frac{1}{4}}/t_{\frac{3}{4}}$ lay very close to the theoretical value of 2·42 for first-order reactions (Table 3). The temperature variation

[13] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 427.
[14] Froemsdorf, Collins, Hammond, and DePuy, *J. Amer. Chem. Soc.*, 1959, **81**, 643.
[15] Anderson and Rowley, *J. Phys. Chem.*, 1943, **47**, 454.
[16] Szwarc, *J. Chem. Phys.*, 1949, **17**, 432.

of the rate constants (Table 4) found by us was expressed as: isopropyl acetate, $k_1 = (2{\cdot}61 \pm 0{\cdot}065) \times 10^{13} \exp\{(-46{,}340 \pm 184)/RT\}$ (sec.$^{-1}$); t-butyl acetate, $k_1 = (1{\cdot}41 \pm 0{\cdot}084) \times 10^{13} \exp\{(-40{,}020 \pm 207)/RT\}$ (sec.$^{-1}$), the error limits being the standard deviations. Both results are in excellent agreement with those of earlier workers.

Kinetics of Pyrolysis of s-Butyl and t-Pentyl Acetate.—By analogy with the stoicheiometry of the decomposition of other acetates, it was assumed that the overall reaction was $CH_3{\cdot}CO{\cdot}OC_nH_{2n+1} \longrightarrow CH_3{\cdot}CO_2H + C_nH_{2n}$. An attempt was made to verify this by a comparison of the percentage reaction [calculated on the basis of $p_t = (2p_0 - P_t)$ where, at time t, p_t is the pressure of acetate and P_t the total pressure, p_0 being the initial pressure] with that derived from direct titration of the acetic acid produced (Table 5).

TABLE 5.

Stoicheiometry of the elimination from s-butyl acetate.

Decomp. (%) (press.)	12·8	23·4	37·9	56·2	75·8	86·0	89·5
Decomp. (%) (anal.)	14·9	24·1	42·5	56·0	76·5	87·2	88·5

This procedure was not found possible for t-pentyl acetate.

Two further observations support the proposed stoicheiometry, namely, the ratio of final to initial pressure, which should be 2 for the proposed stoicheiometry (Table 6), and the fact that first-order plots of log $(2p_0 - P_t)$ against time were linear for >75% decomposition. The

TABLE 6.

The ratio of final to initial pressure.

	s-Butyl acetate			t-Pentyl acetate			
Temp.	303°	321°	329°	239°	247°	280°	290°
p_0 (mm.)	138	198	199	1·01	135	138	139
p_t/p_0	1·87	1·97	1·94	1·95	1·87	1·86	1·98

departures of the observed values of p_t/p_0 from 2 are attributed to the dead space in the apparatus. The average experimental value of p_t/p_0 differs from the theoretical by 4%.

First-order rate coefficients were calculated on the basis of the proposed stoicheiometry, and their independence of initial pressure was verified (Table 7). The reactions are thus obviously of the first order. This conclusion was confirmed by the values of $t_{\frac{1}{2}}/t_{\frac{1}{4}}$ (Table 8). The mean value lies close to the theoretical value (2·42) for a first-order reaction.

TABLE 7.

First-order rate constants.

s-Butyl acetate at 358·8°.					
p_0 (mm.)	126	143	169	271	341
10^4k_1 (sec.$^{-1}$)	23·5	24·4	24·5	23·5	20·6
t-Pentyl acetate at 238·5°.					
p_0 (mm.)	127	155	208	235	284
10^4k_1 (sec.$^{-1}$)	1·73	1·70	1·74	1·71	1·74

TABLE 8.

The ratios of $t_{\frac{1}{2}}/t_{\frac{1}{4}}$ for acetate pyrolysis.

	s-Butyl acetate at 340°.				*t-Pentyl acetate at* 260°.			
p_0 (mm.)	106	145	232	275	108	130	155	266
$t_{\frac{1}{2}}/t_{\frac{1}{4}}$	2·32	2·45	2·15	2·46	2·44	2·48	2·48	2·47

It was found that the rates of decomposition of the acetates were irreproducible in clean glass vessels, the rate of the reaction often decreasing in successive runs, to a final limiting value. Thus at 252·3° five successive runs in an initially clean vessel gave for 10^4k_1 10·0, 9·0, 7·4, 3·8, and 4·1 sec.$^{-1}$. For this reason, runs were made in vessels which had been seasoned by the products of decomposition of allyl bromide.[17] To test the homogeneity of the reaction under these conditions, the reaction vessel was packed with thin-walled glass tubing to give

[17] Maccoll, *J.*, 1955, 965; Thomas and Maccoll, *J.*, 1955, 979.

a nine-fold increase in surface–volume ratio. The mean values of k_1 for five runs done at 318° with s-butyl acetate and 261° with t-pentyl acetate were $2{\cdot}30 \times 10^{-4}$ sec.$^{-1}$ ($2{\cdot}27 \times 10^{-4}$ sec.$^{-1}$) and $8{\cdot}59 \times 10^{-4}$ sec.$^{-1}$ ($8{\cdot}50 \times 10^{-4}$ sec.$^{-1}$), respectively, the mean value for the unpacked vessel being given here in parentheses. Both reactions are thus homogeneous under the conditions used.

Chain mechanisms are known to occur in the pyrolysis of primary esters (Part I). Thus the Arrhenius parameters for ethyl formate, in a static system,[18] were E 40,010 cal./mole and A $2{\cdot}52 \times 10^9$ sec.$^{-1}$; whereas in a flow system, with toluene as a carrier gas,[2] the values were E 44,140 cal./mole and A $2{\cdot}13 \times 10^{11}$ sec.$^{-1}$. Low A and E values are also characteristic of the pyrolysis of n-propyl formate.[15] However, for isopropyl formate the values of the Arrhenius parameters were the same for pyrolysis in static [15] and dynamic [2] systems. This implies that chains play no significant part in the pyrolysis of isopropyl formate. To verify this for s-butyl and t-pentyl acetate, runs were made in the presence of cyclohexene, which has proved effective in inhibiting chain reactions in pyrolysis of alkyl bromides.[8,19] Mean values of the rate constants in the presence and in the absence of cyclohexene (Table 9) show that the reactions are not inhibited by it. It is concluded that the reactions are unimolecular, as proposed by Hurd and Blunck.[20]

TABLE 9.

The lack of effect of cyclohexene on acetate pyrolysis.

	s-Butyl acetate			*t-Pentyl acetate*		
Temp.	303°	339·3°	358·8°	243·6°	278·8°	289·4°
10^4k_1 (sec.$^{-1}$) (no cyclohexene)	0·67	7·27	23·9	3·18	30·3	60·9
10^4k_1 (sec.$^{-1}$) (with cyclohexene)	0·66	7·06	23·6	3·04	29·9	60·0

The effect of temperature upon the rate constants for elimination is shown in Table 10. These results were fitted to the Arrhenius equations: s-butyl acetate, $k_1 = (2{\cdot}00 \pm 0{\cdot}098) \times 10^{13} \exp\{(-46{,}600 \pm 270)/\boldsymbol{RT}\}$; t-pentyl acetate, $k_1 = (2{\cdot}69 \pm 0{\cdot}048) \times 10^{13} \exp\{(-40{,}260 \pm 116)/\boldsymbol{RT}\}$.

TABLE 10.

The effect of temperature on k_1 for elimination.

s-Butyl acetate.

Temp.	303·0°	316·1°	318·9°	321·4°	329·2°	339·3°	350·0°	358·8°
No. runs	6	4	4	5	6	8	6	6
10^4k_1 (sec.$^{-1}$)	0·565	1·63	2·09	2·29	3·79	7·25	13·7	23·3

t-Pentyl acetate.

Temp.	227·1°	238·5°	246·6°	259·5°	267·6°	278·8°	289·4°
No. runs	7	7	7	9	8	7	7
10^4k_1 (sec.$^{-1}$)	0·683	1·71	3·18	8·09	14·6	30·3	60·9

TABLE 11.

Olefin proportion in elimination from acetates.

s-Butyl acetate.

Temp.	303°	316°	319°	321°	339°	350°	359°
But-1-ene (%)	55·9	54·6	55·4	61·0	56·1	52·5	59·0

t-Pentyl acetate.

Temp.	228°	239°	247°	260°	279°	289°
2-Methylbut-1-ene (%)	71·0	77·0	73·8	77·6	76·0	77·0

Products of Pyrolysis.—The olefinic fractions from the kinetic runs were analysed by vapour-phase chromatography. The results confirm that elimination follows the Hofmann rule (Table 11). Of the but-2-ene, the mean percentage of the *trans*-form was 64%, a value close to the

[18] Makens and Eversole, *J. Amer. Chem. Soc.*, 1939, **61**, 3203.
[19] Maccoll and Thomas, *J.*, 1957, 5033; Kale and Maccoll, *J.*, 1957, 5020; Kale, Maccoll, and Thomas, *J.*, 1958, 3016; Harden and Maccoll, *J.*, 1959, 1197.
[20] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.

equilibrium value, which is (62 ± 1)% in the temperature range 300—350°.[21] Anderson *et al.*[22] have measured the rate of the homogeneous conversion of *cis*- into *trans*-but-2-ene. Calculation shows that at the highest temperature used in this investigation, the half-life would be of the order of 80 days. Therefore, either the equilibrium *cis–trans*-mixture is formed at the instant of reaction, or the equilibrium is established rapidly on the carbonaceous coating of the reaction vessel. Evidence presented in Part II suggests that the latter view is correct. The results in Table 12 show that the percentage of 2-methylbut-1-ene is not dependent on

TABLE 12.

Olefin composition at varying percentage decomposition (at 261°).

p_0 (mm.)	164	161	141	139	220	183
Decomp. (%)	24·1	33·2	56·5	73·5	78·0	84·3
2-Methylbut-1-ene (%)	74·9	71·3	69·5	72·8	74·0	73·0

percentage decomposition. This suggests that the olefin ratio is characteristic of the elimination and does not undergo subsequent change. To verify this some but-1-ene was left in the reaction vessel, together with acetic acid, for more than 18 hours at 360°. The extent of isomerisation was not more than 4%. As Bailey *et al.*[23] suggested that carbonaceous surfaces may catalyse olefin isomerisation, a number of runs were made in a flow system—a clean glass reaction vessel packed with glass helices. There was no significant departure from results obtained at lower temperatures in the static experiments. Thus for s-butyl acetate at 451° in the flow system, the mean value from a number of runs was 52·4% of but-1-ene: the value 56% was obtained from the static experiments at 300—360°. For t-pentyl acetate, the flow experiments yielded a value of 73% of 2-methylbut-1-ene; it was 75% in static experiments at 230—290°. Elimination from acetates thus follows the Hofmann rule predominantly, but not exclusively.

DISCUSSION

The secondary and tertiary acetates studied all decompose in seasoned vessels by a homogeneous, unimolecular elimination to an olefin, or a mixture of olefins, and acetic acid. There is no evidence of heterogeneous reactions, although these do occur in unseasoned vessels. Nor is there evidence that reaction chains played a significant part in the elimination. The reactions are all very clean, with no trace of side reaction detectable. The Arrhenius parameters are tabulated (Table 13) and the very similar A factors confirm a common mechanism, namely, unimolecular elimination.

TABLE 13.

The Arrhenius parameters for some acetate eliminations.

Acetate	log A	E (kcal./mole)	Acetate	log A	E (kcal./mole)
Isopropyl [2]	13·00	45·00	t-Butyl [4]	13·34	40·50
	13·42	46·34		13·15	40·02
s-Butyl	13·30	46·60	t-Pentyl	13·43	40·26

In order to estimate the effect of β-methyl substitution, relative rates have been calculated at the temperature at which the symmetrical compound has a rate constant of 10^{-4} sec.$^{-1}$. The relative rates are, s-butyl/isopropyl 0·96 (at 308°) and t-pentyl/t-butyl, 1·50 (at 237°). Thus in the secondary compounds there is a barely significant decrease, while in the tertiary series there is a slight but significant increase. And, just as for α-methylation, the effect is less than for alkyl halides. But it is important that the presence of an α-methyl group enhances the effect of a β-methyl group, suggesting that in the tertiary series the electron demands in the transition state are becoming more like those in the transition states of the halides.

The olefin proportions reported here are in good agreement with those given by other workers. Froemsdorf *et al.*[14] report an average value of 57% of but-1-ene from s-butyl

[21] "Selected Values of the Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.
[22] Anderson, Bell, Diamond, and Wilson, *J. Amer. Chem. Soc.*, 1958, **80**, 2384.
[23] Bailey, Rosenberg, and Young, *J. Amer. Chem. Soc.*, 1955, **77**, 1163.

acetate and 76% of 2-methylbut-1-ene from t-pentyl acetate, the present mean values being 56·3% and 75·3%, respectively.

By using the figures for the percentage composition of the olefins, the rate of elimination into each of the branches may be calculated. The results (Table 14) show that in both

TABLE 14.

Rates of elimination per branch.

Temp.	10^4k_1 left branch	Ester	10^4k_1 right branch
308°	0·50	CH_3–CH(OAc)–CH_3	0·50
308	0·42	CH_3·CH_2–CH(OAc)–CH_3	0·54
237	0·33	CH_3–C(OAc)$(CH_3)_2$	0·33
237	0·37	CH_3·CH_2–C(OAc)$(CH_3)_2$	0·57

cases the rate of elimination into the shorter branch is increased by β-methylation, while the rate of elimination into the longer branch is decreased in the case of the s-butyl compound and increased in the case of the t-pentyl compound. This again suggests that the tertiary acetates have electron demands in the transition state differing somewhat from those of the secondary compounds.

The implications of these results as regards the nature of the transition state for gas-phase elimination from esters will be discussed in a later paper.

EXPERIMENTAL

A commercial sample of isopropyl acetate was fractionated through a 5 ft. vacuum-jacketed column packed with glass helices, the fraction boiling at 88·8°/760 mm. (lit.[24] 89·2°) being collected. t-Butyl acetate was prepared from t-butyl alcohol and acetyl chloride and was carefully fractionated; it had b. p. 97·5°, n_D^{25} 1·3846 (lit.,[24] b. p. 97·0°, n_D^{25} 1·3848). s-Butyl acetate was prepared from s-butyl alcohol and glacial acetic acid, both of which had been previously fractionated. After fractionation it had b. p. 111—112°, n_D^{25} 1·3866 (lit.,[24] b. p. 112—113°, n_D^{25} 1·3865). t-Pentyl acetate, prepared by the method used for t-butyl alcohol, had n_D^{25} 1·3960 (lit.,[25] n_D^{20} 1·4052); vapour-phase chromatography on a dinonyl phthalate column showed it to be more than 99·5% pure. A commercial sample of cyclohexene, shaken with sodium hydrogen sulphite to remove peroxides, dried ($CaCl_2$), and distilled in an atmosphere of nitrogen, had b. p. 84°, n_D^{25} 1·4396 (lit.,[26] b. p. 83°, n_D^{25} 1·4451).

As the reaction produced an increase in pressure, at constant volume, the runs were followed by pressure measurement in an all-glass reaction vessel, as previously described.[17] Acetic acid was estimated by titration with standard sodium hydroxide (phenolphthalein). The chromatographic column used in this investigation contained ethyl acetoacetate on Celite as the stationary phase, at 4°. The olefins were identified by comparison with pure samples.

One of us (E. U. E.) thanks the Government of the Western Region of Nigeria for a Research Studentship. The other (A. M.) thanks the Principal and Professor C. W. L. Bevan of University College, Ibadan, for hospitality. Both thank the British Petroleum Company for a gift of pure olefins, Mr. B. Roberts and the University of London Computer Unit for programming and running the statistical calculations, and the University of London Research Grant Committee for grants to Professor Dame Kathleen Lonsdale for the purchase of tape-editing equipment and to A. M. for the purchase of a recording potentiometer.

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[*Received, July* 31*st*, 1961.]

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