

37. *Gas-phase Eliminations. Part VI.* The Pyrolysis of 1-Methylbut-3-enyl and 1-Methyl-3-oxobutyl Acetate.*†

By E. U. EMOVON and ALLAN MACCOLL.

Pyrolysis of 1-methylbut-3-enyl and 1-methyl-3-oxobutyl acetate at 291–355° and 256–297° has been shown to involve homogeneous, unimolecular elimination, with rate constants $k_1 = 1.00 \times 10^{13} \exp(-44,410/RT)$ and $7.60 \times 10^{11} \exp(-37,400/RT)$ sec.⁻¹, respectively. Implications regarding the transition states in ester pyrolyses are discussed.

It was suggested earlier¹ that the transition state in pyrolysis of esters can be regarded as arising from nucleophilic attack by the carbonyl-oxygen atom on the β -hydrogen atom, in a six-atom ring. Viewed in this way, the reaction might be expected to be analogous in some ways with the *E2* reaction in a polar solvent. DePuy *et al.*,² on the other hand, suggest that "the transition state of the acetate pyrolysis reaction is best described as one in which both the C-H and the C-O bonds are to a large extent broken and a great deal of double bond character has developed, but one in which no appreciable charge separation is evident." Smith *et al.*³ maintain that the rate of ester pyrolysis "is influenced by electron release to the carbon-oxygen single bond and by strong electron withdrawal from the β -hydrogen. The character of the bonds being *broken*, particularly the carbon-oxygen bond (and not those being formed), are principally responsible for the stability of the esters. Olefin stability is of little importance in determining the stability of the esters in contrast to the character of the C-O bond . . . the pyrolysis of carboxylic esters proceeds *via* a highly concerted mechanism with simultaneous carbon-oxygen and carbon-hydrogen bond-breaking in the transition state." The present work was undertaken to investigate (a) the effect of homolytic weakening of the β -carbon-hydrogen bond (1-methylbut-3-enyl acetate, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$) and (b) the effect of increasing the acidity of the β -carbon-hydrogen bond (1-methyl-3-oxobutyl acetate,

* Part V, *J.*, 1964, 149.

† Preliminary report, Maccoll in "Theoretical Organic Chemistry," Butterworths, London, 1959.

¹ Maccoll, *J.*, 1958, 3398.

² DePuy, King, and Froemsdorf, *Tetrahedron*, 1959, 7, 123.

³ Smith, Bagley, and Taylor, *J. Amer. Chem. Soc.*, 1961, 83, 3647.

Me·CO·CH₂·CHMe·OAc). There is no reason to assume *a priori* that a decrease in the homolytic bond-dissociation energy $D(\text{R-H})$ of a carbon-hydrogen bond is paralleled by a decrease in the corresponding heterolytic bond-dissociation energy $D(\text{R-H}^+)$. For $D(\text{R-H}^+) = D(\text{R-H}) + I(\text{H}) - I(\text{R}^-)$, where $I(\text{H})$ is the ionisation potential of hydrogen and $I(\text{R}^-)$ is the ionisation potential of the carbanion R^- , that is, the electron affinity of R. Changes in $D(\text{R-H})$ can be counteracted or even outweighed by changes in $I(\text{R}^-)$. Thus the decreases in the homolytic bond-dissociation energies in propene and toluene, as compared with ethane, do not necessarily imply a lowering of the heterolytic dissociation energies of the carbon-hydrogen bonds in these molecules and hence an increased acidity. However, if acetone is compared with toluene, the existence of an enol form suggests that the carbon-hydrogen bonds in the former are more acidic than are those in the latter.

In Parts I¹ and III⁴ the effects of α - and β -methyl substitution upon the rates of elimination from esters has been discussed. An elegant study of the effects of substituents separated from the reaction centre by a benzene ring has been made by Smith *et al.*³ Some semiquantitative work, based mainly on product separation, exists in the literature in the cases of certain other substitutions. For instance, DePuy *et al.*² have shown by a competitive method that α -methylbenzyl acetate is pyrolysed at about the same rate as 1-butylpentyl acetate, whereas the rate for phenethyl acetate is about one-tenth of that for the secondary compound. The small effect of 1-phenyl substitution clearly demonstrates, contrary to the view of DePuy *et al.*, that the forming double bond plays little part in the transition state. This situation is in marked contrast with that obtaining in the case of the halides, for α -methylbenzyl halides decompose at about the same rates as the corresponding tertiary halides, while the phenethyl compounds decompose at about the same rates as the n-propyl halides.⁵ However, Smith *et al.*³ have shown that 1,2-diphenylethyl acetate decomposes somewhat faster than s-butyl acetate, the relative rate of decomposition being 8:1:1 at 350°, as calculated from the Arrhenius equations.

There is often a striking effect of substituents upon product composition. Thus the *trans*-isomer of 2-acetoxycyclohexanecarboxylate gave almost exclusively the conjugated isomer,⁶ while $\alpha\alpha$ -dimethylbenzyl acetate gave 75% of α -methylstyrene.⁷ Again, DePuy *et al.*² have shown that pyrolysis of 1-methoxy-1-methylethyl acetate gives a slightly greater proportion of the internal olefins than does s-butyl acetate. The evidence in the literature thus suggests that the most important effects of substituents observed up to the present are upon product composition, the effect on the rate of elimination being modest. This paper extends the field of substituted esters examined under kinetically controlled conditions.

EXPERIMENTAL

1-Methylbut-3-en-1-ol was prepared by Hoyer's method.⁸ Purified allyl chloride (1 mole) was added to magnesium (1 g.-atom) in sodium-dried ether (400 c.c.) at $-15^\circ \pm 2^\circ$, reaction having been initiated at the b. p. of ether. Purified acetaldehyde (0.7 mole), in an equal volume of ether, was gradually added and the mixture was kept for several hours at -15° . Distilling off the ether and fractionating the residue gave the alcohol, b. p. 115.5°/758 mm., n_D^{25} 1.4230 (lit.,⁸ 115.1°/755 mm., n_D^{25} 1.4220). The acetate, prepared by Pariselle's method,⁹ had b. p. 134.5°/760 mm., n_D^{25} 1.4090 (lit.,⁸ 132—135°/760 mm., n_D^{20} 1.413). Vapour-phase chromatography of our ester showed it to be at least 99.5% pure.

1-Methyl-3-oxobutyl alcohol was prepared by condensing redistilled acetone and acetaldehyde in the presence of potassium hydroxide in methanol (cf. Dubois¹⁰). Its acetate, obtained by Bergmann and Kann's method,¹¹ had b. p. 93°/22 mm., n_D^{22} 1.4191 (lit.,¹¹ 84°/12 mm.).

⁴ Emovon and Maccoll, *J.*, 1962, 335.

⁵ Stephenson, Ph.D. Thesis, London, 1957.

⁶ Bailey and Baylouny, *J. Amer. Chem. Soc.*, 1959, **71**, 6443.

⁷ Bailey and King, *J. Org. Chem.*, 1956, **21**, 858.

⁸ Hoyer, Ph.D. Thesis, London, 1953.

⁹ Pariselle, *Compt. rend.*, 1912, **154**, 710.

¹⁰ Dubois, *Bull. Soc. chim. France*, 1949, 66.

¹¹ Bergmann and Kann, *Annalen*, 1924, **438**, 290.

Cyclohexene, used in the inhibition experiments, was purified as described earlier.⁴

The rate of reaction was measured in an all-glass system as described earlier.¹²

Rate Measurements.—Measurements of the rate of reaction were made in vessels which had been seasoned by the products of decomposition of allyl bromide.^{12,13} By analogy with the behaviour of other esters, the stoichiometry $\text{Me}\cdot\text{CO}_2\text{R} \rightarrow \text{Me}\cdot\text{CO}_2\text{H} + \text{Ol}$, where Ol is an olefinic species, was assumed. An attempt was made to verify this by (a) measurements of P_t/p_0 where P_t is the final and p_0 the initial pressure, which should be 2 on the basis of the proposed scheme (Table 1), and (b) comparison of the percentage decomposition determined from $p_t = (2p_0 - P_t)$ where p_t is the pressure of ester and P_t the total pressure, both at time t , with that from analysis (Table 2).

TABLE 1.
Stoichiometry of the decomposition.

	$\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$			$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$		
Temp.	346°	324°	311°	286°	267°	256°
p_0 (mm.)	159	146	112	98	135	198
P_t/p_0	1.88	1.68	1.75	1.95	1.91	1.91

TABLE 2.
Decomposition (%) of 1-methylbut-3-enyl acetate.

Decomp. (%) (press.)	21.9	27.4	46.8	69.4	84.9
Decomp. (%) (anal.)	24.5	27.1	51.7	75.8	90.1

The results in Table 1 confirm the stoichiometry in the second case. In the first, the fact that $P_t/p_0 < 2$ can be attributed to polymerisation of the diolefin produced during the long time required to obtain the P_t values. This view was confirmed by the presence of a green substance in the condensed products of prolonged reaction (also see below). The agreement in Table 2 is not good, the percentage decomposition estimated by titration (with standard alkali) of the acetic acid produced being greater than that estimated from pressure measurements. This is possibly due to base-catalysed hydrolysis of the undecomposed ester. The fact that pressure measurements give a faithful measure of the degree of decomposition is confirmed, as will be shown below, by the linearity of the first-order plots up to at least 75% reaction; this would not be so were the stoichiometry to differ from that proposed.

The homogeneity of the reaction was verified (see Table 3) by runs in a vessel of which the surface : volume ratio had been increased by a factor of nine over that for the empty vessel. The values for the empty vessel were obtained from the Arrhenius equations; those for the packed vessel are the means of about six runs.

TABLE 3.
Homogeneity of the reaction.

$\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$			$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$		
Temp.	10^4k_1 (P) *	10^4k_1 (E) †	Temp.	10^4k_1 (P) *	10^4k_1 (E) †
320.9°	4.52	4.48	278.3°	10.8	10.1
304.7	1.60	1.55			

* Packed vessel. † Empty vessel.

TABLE 4.
First-order rate constants.

$\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$, at 334.3°					
p_0 (mm.)	89.3	103.5	169.5	211.3	302.3
10^4k_1 (sec. ⁻¹)	10.4	10.4	10.9	10.6	10.7
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OAc}$ at 256.4°					
p_0 (mm.)	81.7	81.7	164.2	230.5	245.4
10^4k_1 (sec. ⁻¹)	2.92	2.65	2.74	2.82	2.92

The first-order character of the decomposition was verified by the fact that the rate coefficients calculated from a plot of $\log(2p_0 - P_t)$ were independent of initial pressure (Table 4).

¹² Maccoll, *J.*, 1955, 965.

¹³ Maccoll and Thomas, *J.*, 1955, 979.

The variation of the rate constants with temperature (Table 5) was expressed by the Arrhenius equations: (a) $k_1 = (1.00 \pm 0.12) \times 10^{13} \exp(-44,400 \pm 132)/RT$; (b) $k_1 = (7.60 \pm 0.15) \times 10^{11} \exp(-37,400 \pm 433)/RT$, the error limits being the standard deviations. In both cases the experimental points were well represented by these equations.

TABLE 5.
Variation of the rate constants with temperature.

(a) CH ₂ :CH·CH ₂ ·CHMe·OAc							
Temp.	291.6°	301.9°	311.5°	324.4°	333.4°	346.3°	355.1°
No. of runs	6	6	7	7	11	7	9
10 ⁴ k ₁ (sec. ⁻¹)	0.65	1.28	2.47	5.62	10.6	21.5	34.6
(b) CH ₃ ·CO·CH ₂ ·CHMe·OAc							
Temp.	256.4°	267.2°	278.3°	286.2°	297.7°		
No. of runs	5	7	7	6	6		
10 ⁴ k ₁ (sec. ⁻¹)	2.81	5.70	10.8	18.9	36.7		

While primary esters have been observed to be pyrolysed by a chain mechanism,^{14,15} secondary esters are pyrolysed by unimolecular mechanisms.¹⁵⁻¹⁷ 1-Methylbut-3-enyl acetate was pyrolysed in the presence of cyclohexene, which has been shown to inhibit chains in bromide pyrolyses.¹⁸ The means of a number of runs done at 301.9° and 355.1° were $1.22 \times 10^{-4} \text{ sec.}^{-1}$ ($1.28 \times 10^{-4} \text{ sec.}^{-1}$) and $34.3 \times 10^{-4} \text{ sec.}^{-1}$ ($34.6 \times 10^{-4} \text{ sec.}^{-1}$), the values in parentheses being calculated from the Arrhenius equations for reactions in the absence of cyclohexene. There is thus no inhibition.

The unsaturated products of elimination were studied by vapour-phase chromatography. The products from 1-methylbut-3-enyl acetate were *cis*- and *trans*-penta-1,3-diene and penta-1,4-diene. Results of a number of runs (Table 6) yielded mean values of 19%, 46%, and 35%,

TABLE 6.
Composition of olefins formed by pyrolyses of 1-methylbut-3-enyl acetate.

<i>cis</i> -Pent-1,3-diene (%)	20	16	22	18	18	19	23
<i>trans</i> -Pent-1,3-diene (%)	44	44	46	45	50	50	41
Pent-1,4-diene (%)	36	40	32	37	32	31	36

respectively. As distinct from the case of *s*-butyl acetate,⁴ *cis*- and *trans*-penta-1,3-diene are not produced in equilibrium amounts. The mean percentage of the *trans*-compound found experimentally was 70%, the equilibrium percentage in the temperature range 400–600°K can be calculated as 42%. These results show that there is a tendency for the conjugated olefins to be formed. Results of prolonged experiments confirm the explanation given for the P_f/p_o values of <2: when the reaction mixture was left in the vessel overnight, the percentage of penta-1,4-diene was from 35–65; when the mixture was left over a week-end this amount had risen to 76%. Since penta-1,3-diene is the thermodynamically stable isomer, the change can only imply its disappearance, probably by polymerisation. In the case of 1-methyl-3-oxobutyl acetate, only one product was observed on vapour-phase chromatography, namely, pent-3-en-2-one; the column used was not capable of resolving the *cis*- and *trans*-forms of this compound.

DISCUSSION

1-Methylbut-3-enyl and 1-methyl-3-oxobutyl acetate are pyrolysed in seasoned vessels to give, respectively, a mixture of pentadienes and pent-3-en-2-one. The reactions are homogeneous and follow first-order laws, the rate coefficients being independent of initial pressure. At no time were induction periods observed, and with the unsaturated acetate elimination took place at the same rate in the presence as in the absence of cyclohexene,

¹⁴ Makens and Eversole, *J. Amer. Chem. Soc.*, 1939, **61**, 3203.

¹⁵ Anderson and Rowley, *J. Phys. Chem.*, 1943, **47**, 454.

¹⁶ Blades, *Canad. J. Chem.*, 1954, **32**, 366.

¹⁷ Barton, Head, and Williams, *J.*, 1953, 1715.

¹⁸ Maccoll and Thomas, *J.*, 1957, 5033.

a good inhibitor for radical-chain reactions.¹⁸ The frequency factors of the Arrhenius equations are within the range found by other workers in the field of ester pyrolyses and are close to the "normal" value for a unimolecular reaction. It is concluded that both compounds decompose by the unimolecular mechanism.

For 1-methylbut-3-enyl acetate the Arrhenius parameters, E 44.4 kcal. mole⁻¹ and A 1.00×10^{13} sec.⁻¹, are close to those for *s*-butyl acetate,⁴ namely, E 46.6 kcal. mole⁻¹ and A 2.00×10^{13} sec.⁻¹. For 1-methyl-3-oxobutyl acetate parameter E is 37.4 kcal. mole⁻¹ and A 7.6×10^{11} sec.⁻¹, so that the large decrease in activation energy is in part compensated by a decrease in the A factor. The rates of elimination per branch are shown in Table 7. In each case the effect of substitution is to increase the rate of elimin-

TABLE 7.
Rates of elimination per branch (temp. 309°).

$10^4 k_1$ (sec. ⁻¹), left branch	Ester	$10^4 k_1$ (sec. ⁻¹), right branch
0.44	Me·CH ₂ ·CHMe·OAc	0.56
1.29	CH ₃ :CH·CH ₂ ·CHMe·OAc	0.73
106 *	CH ₃ ·CO·CH ₂ ·CHMe·OAc	2.2 *

* Calculated on the assumption that 2% of pent-1-en-4-one could have been detected.

ation from the longer branch. But whereas the effect of the vinyl group is small, that of the acetyl group is large, the keto-ester decomposing at some 108 times as rapidly as *s*-butyl acetate at 309°. The effect of the acetyl group is also apparent for pyrolysis of acetic anhydride, studied by Szwarc and Murawski,¹⁹ which at 355° undergoes pyrolysis at a rate 13,000 times faster than ethyl acetate. The carbonyl group thus has a much greater effect in the α - than in the γ -position and both compounds illustrate that increasing the acidity of the β -hydrogen atom increases the rate of pyrolysis.

General.—As pointed out earlier,¹ while primary esters possessing a β -carbon-hydrogen bond tend to decompose by a mixed radical-chain and unimolecular mechanism, secondary and tertiary esters of the same type decompose by a purely unimolecular mechanism. Pyrolysis of the primary esters thus usually has to be studied in the presence of an inhibitor in order to isolate the unimolecular reaction. The Arrhenius parameters for the unimolecular pyrolysis of esters are gathered in Table 8. The Figure shows a plot of the activation energy against the temperature at which the rate constants have a value of 10^{-4} sec.⁻¹, this value being chosen since it corresponds to a half-life of about 2 hr. and so is almost certain to be included in the range studied experimentally in static systems. Several matters of interest emerge. First, the points for fourteen of the compounds lie reasonably close to a straight line, showing that changes in rate, at least for simple aliphatic esters, are in the main due to changes in activation energy. Secondly, there are five exceptions to this, namely, ethyl and *t*-butyl formate, menthyl benzoate, 1-methyl-3-oxobutyl acetate, and acetic anhydride; for the first three it is probable that both A and E are too low, since the points for all the other simple aliphatic esters lie relatively close to the line; for the remaining two, some special factor probably operates, being due to the very powerful influence of the carbonyl group. This is discussed below. Thirdly, di-2-ethylhexyl sebacate decomposes²¹ in the liquid phase at roughly the same rate as the inhibited decompositions of the other primary esters; the Arrhenius parameters in no way suggest a chain mechanism, and this can be explained in terms of the number of carbon-hydrogen bonds of nearly equal strength, of which only four are β to the carboxylate group; thus in any chain process the chance of hydrogen abstraction at a β -carbon atom would be small and so stopping radicals, which are incapable of propagating the chain, would be predominantly produced.²⁸ With primary bromides, a similar effect was

¹⁹ Szwarc and Murawski, *Trans. Faraday Soc.*, 1951, **47**, 268.

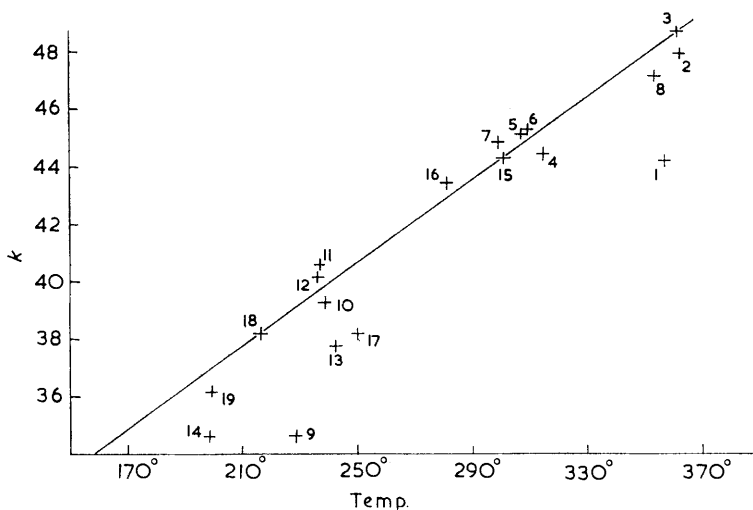
²⁰ Blades, personal communication to DePuy, quoted by DePuy and King, *Chem. Rev.*, 1960, **60**, 431.

TABLE 8.

Arrhenius parameters for ester pyrolyses.

Compound	E (kcal. mole ⁻¹)	$10^{-12} A$ (sec. ⁻¹)	Ref.	Compound	E (kcal. mole ⁻¹)	$10^{-12} A$ (sec. ⁻¹)	Ref.
Primary				Secondary			
Et formate	44.1	0.21	16	Pr ⁱ formate	44.2	2.70	16
Et acetate	48.0	5.00	16	Pr ⁱ acetate	44.0	3.80	15
Et propionate	48.5	5.20	20	Bu ^s acetate	45.0	10.00	16
Di-2-ethylhexyl sebacate	47.1	2.70	21	CH ₂ :CH·CH ₂ :CHMe·OAc	46.3	13.42	4
Acetic anhydride	34.5	1.26	22	CH ₃ :CO·CH ₂ :CHMe·OAc	46.6	13.30	4
Tertiary				Cholesterol acetate	44.4	10.00	*
Bu ^t formate	34.6	0.13	22	Menthyl benzoate	37.4	80.76	*
Bu ^t acetate	40.5	21.90	23	CH ₂ Ph·CHPh acetate	44.1	5.00	25
Bu ^t propionate	40.5	19.50	4		38.1	0.10	27
CMe ₂ Et acetate	40.5	19.50	4		43.3	11.20	3
Bu ^t chloroacetate	39.2	6.30	24				
Bu ^t dichloroacetate	40.1	22.40	4				
	38.1	12.30	26				
	36.1	5.89	26				

* This paper.



Activation energy as a function of the temperature at which the velocity constant has a value of 10^{-4} sec.⁻¹. (1) Et formate; (2) Et acetate; (3) Et propionate; (4) Prⁱ formate; (5) Prⁱ acetate; (6) Bu^s acetate; (7) 1-methylbut-3-enyl acetate; (8) di-2-ethylhexyl sebacate; (9) Bu^t formate; (10) Bu^t acetate; (11) Bu^t propionate; (12) t-pentyl acetate; (13) 1-methyl-3-oxobutyl acetate; (14) acetic anhydride; (15) cholesteryl acetate, (16) 1,2-diphenylethyl acetate; (17) menthyl benzoate; (18) Bu^t chloroacetate; (19) Bu^t dichloroacetate.

noticed, namely, that the chain contribution to the overall rate diminished down the homologous series from ethyl to n-hexyl.²⁹ Fourthly, despite the molecular complexity of cholesterol acetate, and the fact that it was studied in the liquid phase, the corresponding point fits nicely in the region of the points for the remaining secondary acetates.

²¹ Sommers and Crowell, *J. Amer. Chem. Soc.*, 1955, **77**, 5443.

²² Gordon, Price, and Trotman-Dickenson, *J.*, 1957, 2813.

²³ Rudy and Fugassi, *J. Phys. Chem.*, 1948, **52**, 357.

²⁴ Warwick and Fugassi, *J. Phys. Chem.*, 1948, **52**, 7314.

²⁵ O'Connor and Nace, *J. Amer. Chem. Soc.*, 1953, **75**, 2118.

²⁶ Barton, Head, and Williams, *J.*, 1953, 1715.

²⁷ Emovon, *J.*, 1963, 1246.

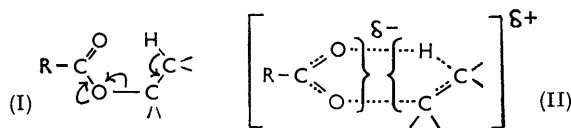
²⁸ Agius and Maccoll, *J.*, 1955, 973; Maccoll and Thomas, *J.*, 1955, 979.

²⁹ Green, Maccoll, and Thomas, *J.*, 1960, 184.

Most of the esters studied fit into three classes, depending on whether they are derived from primary, secondary, or tertiary alcohols. The activation energies in the three cases are 48 ± 1 , 45 ± 1 , 38 ± 2 kcal. mole⁻¹ and the gaps are sufficiently wide, in the absence of special structural features, to enable the rate of dehydrocarboxylation to be diagnostic of the type of parent alcohol.

The substituent effects may be discussed in terms of (a) the strength of the acid from which the ester is derived, (b) the acidity of the β -carbon-hydrogen bond, and (c) the stability of the olefins formed. They may be interpreted in terms of the effect on (d) the breaking carbon-hydrogen or forming oxygen-hydrogen bond or (e) the breaking alkyl-oxygen bond.

Strength of the acid. Smith and Wetzel³⁰ showed qualitatively that the stronger the acid the faster is its pyrolysis. Emovon²⁷ showed that for the series t-butyl acetate, chloroacetate, and dichloroacetate the log of the rate constant is linearly related to the p*K* of the acid. Since the greater the strength of the acid, the greater the electron-withdrawal from the oxygen attached to the hydrogen, it appears that this effect must be interpreted as a weakening of the alkyl-oxygen bond, with a relayed effect on the β -carbon-hydrogen



bond through the virtual carbonium ion, as represented in (I) and (II). Both effects would tend to increase the rate of elimination. The result should be most apparent in those esters derived from alcohols whose alkyl radicals can form very stable carbonium ions.

Acidity of the β -carbon-hydrogen bond. Smith *et al.*³ have shown that in the system $X \cdot C_6H_4 \cdot CH(OAc) \cdot CH_2 \cdot C_6H_4 \cdot Y$ electron-withdrawing substituents Y increase the rate of elimination, whereas electron-donating substituents Y tend to decrease it. But the effect is very small, both on the rate and on the acidity of the β -hydrogen atoms as estimated from nuclear magnetic resonance spectra. The increased rate of pyrolysis of acetic anhydride over that of ethyl acetate was interpreted as being due to the increased acidity of the β -hydrogen atom. There is obviously a further factor at work in this case, for the rate ratio, 1-methyl-3-oxobutyl acetate : s-butyl acetate, observed here, namely 108 (at 309°), is much less than that observed for acetic anhydride : ethyl acetate,¹⁹ namely, 13,000 (at 355°). The present work clearly illustrates the marked effect of the acidity of the β -hydrogen atoms in increasing the rate, for the γ -carbonyl group should have only a negligible effect on the heterolysis of the alkyl-hydrogen bond.

Effect of olefin stability.—The stability of the derived olefin affects the rate of reaction in two ways. Increasing stability will tend to decrease the heterolytic dissociation energy of the alkyl-oxygen bond through stabilisation of the carbonium ion and will also decrease that of the β -carbon-hydrogen bond, owing to the increasing importance of contributions by structures of the type $RR'C(H^+):CR''R'''$ in the ion. This accounts for the relatively small but significant effect of α -methyl substitution. For halides, where heterolysis is much more important, the effect of α -methyl substitution is also much greater.³¹ The same effect is shown in the case of phenyl-substitution. For, whereas α -methylbenzyl halides are pyrolysed at about the same rate as the corresponding t-butyl halide, that is, nearly 200 times as fast as the isopropyl halide, 1,2-diphenylethyl acetate decomposes only eight times as fast as s-butyl acetate.³ It can be concluded, with Smith *et al.*,³ that olefin stability is "of little importance in determining the stability of esters."

The effect of deuteration on the rate has been investigated by a number of workers

³⁰ Smith and Wetzel, *J. Amer. Chem. Soc.*, 1957, **79**, 875.

³¹ Maccoll, "Theoretical Organic Chemistry," Butterworths, London, 1960, p. 230.

(references will be found in ref. 32) who agree on a value of k_H/k_D close to 2 in the range 400–500°. This is near the maximum value for the loss of a carbon–hydrogen stretching vibration in the transition state, namely, 2.3 at 400° and 2.1 at 500°. ³² If the effect is attributed to a single carbon–deuterium bond, then this bond must be very nearly broken in the transition state, as DePuy and King ³³ have concluded. If, on the other hand, all the carbon–deuterium bonds are considered and the effects of hyperconjugation and rehybridisation in the transition state are taken into account, there is no need to postulate nearly complete breaking.

The direction of elimination from esters has been fully discussed by DePuy and King ³³ and will not be further analysed here.

The conclusion to be drawn from this discussion is that, contrary to the views expressed in Part I,¹ both the ease of breaking of the alkyl–oxygen bond and the ease of breaking of the β -carbon–hydrogen bond in the heterolytic sense are of importance in increasing the rate of pyrolysis of esters, in agreement with the views of other authors.^{3,33} The unimolecular decomposition of esters is thus best thought of as a quasiheterolytic reaction of much the same type as the unimolecular decomposition of alkyl halides, but as one in which substituent effects on the heterolysis of the alkyl–oxygen bond are greatly reduced.

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. We also acknowledge helpful discussion with Professor V. R. Stimson.

DEPARTMENT OF CHEMISTRY, UNIVERSITY COLLEGE,
IBADAN, NIGERIA.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE,
GOWER STREET, LONDON W.C.1.

[Received, May 27th, 1963.]

³² Wiberg, *Chem. Rev.*, 1955, **55**, 713.

³³ DePuy and King, *Chem. Rev.*, 1960, **60**, 431.
