

Thermolytic Reactions of Esters. Part 12.¹ Steric versus Polar Effects in Pyrolytic β -Elimination of Acetic Acid from (Tertiary) Alkyl Acetates ¹

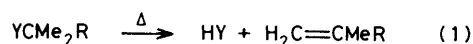
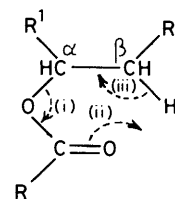
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The vapour-phase pyrolysis of the crowded tertiary alkyl acetates $\text{AcOCMe}_2\text{Bu}^t$ (II) and AcOCMePr^i_2 (III) to give acetic acid and the appropriate alkene(s) has been studied. Rates of formation of alk-1-ene and of isobutene from t-butyl acetate were compared. On this basis steric acceleration in pyrolysis of AcOR , employing known steric parameters E_s^* from groups R, is quantitatively analysed. Although the steric effect can be quite substantial, the remarkable rate increase in the series $\text{AcOEt}-\text{AcOPr}^i-\text{AcOBu}^t$ is largely due to a polar effect. A rationale is presented for the apparent inconsistency: the rate effect of α -alkylation in R is even larger than that in S_N1 -type solvolysis of RBr , suggesting a large charge separation AcO^- , R^+ in the transition state for concerted β -elimination, whereas the Hammett ρ value observed for pyrolysis of e.g. $\text{AcOCH}(\text{Me})\text{C}_6\text{H}_4\text{Z}$ is only a few percent of that associated with formation of benzylic carbenium ions.

The mechanism of the (vapour-phase) thermolysis of esters, to give alkene(s) and carboxylic acid, has been extensively studied and discussed.² Structural effects mostly are in line with a one-step, homogeneous reaction involving a six-membered cyclic transition state, albeit with distinct heterolytic character.²⁻⁵ In the transition state, movement of the electron pairs, in general, proceeds in the order (i) > (ii) > (iii).^{5a} This would result in a somewhat negatively charged RCO_2 group, give some carbenium-ion character to α -C, and result in a somewhat negatively charged β -C atom. Reversible formation of (intimate) ion pairs, RCO_2^- , alkyl^+ , was advanced some time ago^{2a,6} in order to explain certain polar substituent effects. There is no experimental justification, however, for this alternative mechanism.^{3,4,7}

Nevertheless, transition state properties (free energy content, charge distribution) are clearly dependent on substituents.² For example, replacement of $\text{R}^2 = \text{H}$ by acetyl in acetates ($\text{R} = \text{CH}_3$) leads to a $>10^2$ -fold increase in rate at 300 °C, if $\text{R}^1 = \text{H}$ or alkyl.⁸ One of the most striking features is the large rate increase in the series primary, secondary, tertiary alkyl acetates. At 600 K AcOBu^t eliminates ca. 3 300 times as fast as AcOEt .^{5c} Extrapolated to room temperature, this is $>10^6$:1, an effect not unlike those encountered in S_N1-E1 solvolytic reactions. The difference in activation energy for the two acetates amounts to ca. 30 kJ mol^{-1} ,^{5c} quite substantial when compared with the difference in gas-phase ionization energies for AcOEt and AcOBu^t to give $\text{AcO}^- + \text{R}^+$, ca. 150 kJ mol^{-1} .[†]

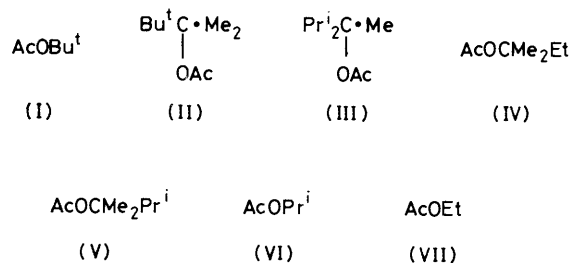
Comparable results were obtained with benzoates.^{2,5} Yet, for substituted benzoates $\text{ZC}_6\text{H}_4\text{CO}_2\text{R}^1$, Hammett ρ values at 600 K are only +0.26 ($\text{R}^1 = \text{Et}$), +0.335 ($\text{R}^1 = \text{Pr}^i$), and +0.58 ($\text{R}^1 = \text{Bu}^t$).⁵ Even for phenylethyl acetates $\text{AcOCH}(\text{Me})\text{C}_6\text{H}_4\text{Z}$, benzylic compounds which should therefore be as 'good' as AcOBu^t in stabilizing a positive charge developing at the α -carbon, ρ is -0.63 at 625 K,^{5b} i.e., ca. -1.3 at 298 K. Note that the operation of fully charged intermediates in the gas phase is associated with ρ values as large as (-) 20.¹¹ Smith and Kelly^{2b} have already remarked that Hammett ρ values for ester pyrolysis are 'surprisingly small in view of the marked change brought about in going from 1° to 2° to 3° esters.' Their suggestion, that the rate-determining stage occurs early along the reaction path, is unsatisfactory as



activation barriers are high compared with overall heats of reaction.

Apart from (the range of) polar, electronic effects, one may ask to what degree steric effects play a part. The more crowded the starting ester, the more strain is relieved upon formation of an alkene. Steric acceleration is clearly seen in a number of cases,^{2-4,12,13} both with increasing bulk of R^2 (at β -C) and of R^1 (at α -C). For example, statistically corrected relative rates of formation of alk-1-ene (equation 1; $\text{Y} = \text{AcO}$) at 300 °C are:^{2a} $\text{R} = \text{Me}$ (1), Et (2.6), Pr^i (4.7). (Note that for $\text{R} = \text{H}$, the relative rate is only 0.04.²) Unfortunately, it is not possible to compare this kinetic result with the maximum attainable effect associated with formation of alkenes, as independently determined ΔH_f° and ΔS° values for gaseous esters are, to our knowledge, only available for ethyl and isopropyl acetate.¹⁴

In order to determine to what extent the large rate enhancement in ester pyrolysis, for tertiary versus primary acetates, is due to steric acceleration, we have compared the thermolysis of the very strained tertiary acetates (II) and (III) with that of AcOBu^t (I). This enables us to correlate rates of elimination to give primary alkenes for an extended series of tertiary acetates [equation (2)] with a suitable steric parameter,

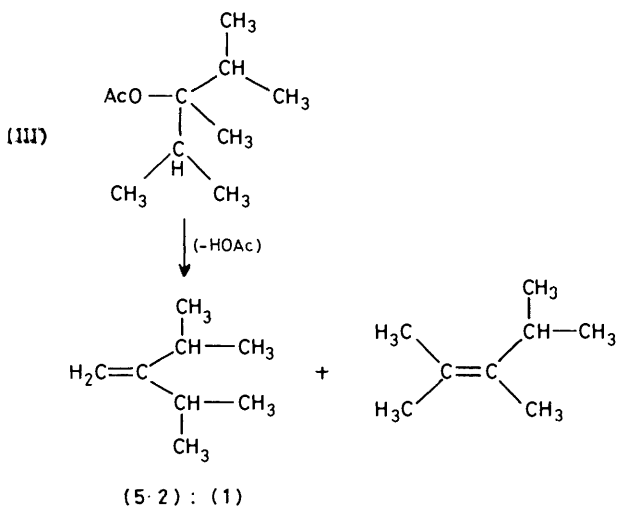
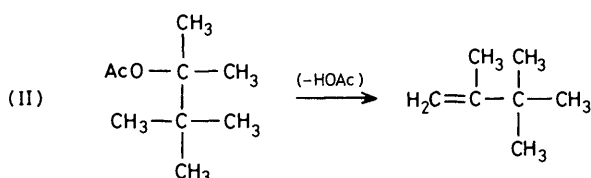
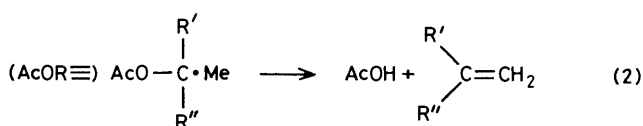


[†] Neglecting minor differences in bond dissociation energies of $\text{AcO}-\text{Et}$ and $\text{AcO}-\text{Bu}^t$ (*vide infra*), and using heats of formation in the gas phase: Et^\cdot (109),^{9a} $\text{Bu}^t\cdot$ (33),^{9b} Et^+ (905),^{10a} and Bu^t+ (678 kJ mol^{-1}),^{10b} one calculates a value of 151 kJ mol^{-1} .

Table 1. Pyrolysis of compounds AcOR^a

R	T/K	log (k/s ⁻¹)	R	T/K	log (k/s ⁻¹)	R	T/K	log (k/s ⁻¹)
Bu ^t ^c	561	-1.86	CMe ₂ Bu ^t ^c	538	-1.73	CMePr ₂	525	-2.00
(I)	563 ^b	-1.84	(II)	548 ^b	-1.51	(III)	538	-1.58
	571	-1.66		551	-1.34		554	-1.16
	582	-1.31		561	-1.09		567	-0.84
	597	-0.99		571	-0.84		581	-0.44
	609	-0.62		582	-0.50		590	+0.23
	617	-0.46						
	627	-0.15						

^a In microreactor (average residence time 4.0 s) unless otherwise stated; log *k* values are averages of duplicate or triplicate runs. Conversions of <15% determined *via* product alkene(s), of >70% based on unconverted ester. For treatment of rate data, *cf.* ref. 16; 95% confidence limits ±0.05 (log *k* < -1.0), up to ±0.08 (log *k* > -1.0). ^b In macroreactor, average residence time 102 ± 2 s; tank-flow kinetics. ^c A competitive run in the macroreactor (105 s, 531 K) gave conversions of AcOBu^t (15.0%) and (II) (51%) and hence log (*k*/s⁻¹) values of -2.77 and -2.00, respectively.

**Scheme 1.**

(-)*E*_s'¹⁵ for the total group R. Typical -*E*_s' values are: Et 0.08; Bu^t 1.43; Pr₂CMe [*cf.* compound (III)] 7.38.¹⁵ Extrapolation to zero steric effect (*E*_s → 0) should lead to the 'true' polar effect of α-alkylation.

Results

Acetates (II) and (III) were prepared from the respective alcohols and ketene.^{7b} The alcohols in turn were synthesized from methyl *t*-butyl ketone and di-isopropyl ketone, respect-

Table 2. Kinetic data on pyrolysis of acetates

Ester	T/K	log (A/s ⁻¹)	<i>E</i> /kJ mol ⁻¹	log <i>k</i> _{rel} ^a	Ref.
(I)	582—627	14.28	175 ^b	(0)	This work
		13.3	169		5c
		13.73	176		7b
		13.15	168		18
(II) (a)	538—582	14.22	165 ^c	0.99	This work
(b)		14.4 ± 0.4	172 ± 4		13a
(III)	525—590	13.9	161 ^d	1.31	This work
(IV) (a)	503—562	13.43	169	0.22	18
(IV) (b)				0.43	2a
(V)		13.96	171	0.61	7b
				0.67	2a
(VI)	609—668	13.2	192	-1.9	5c
(VII)	650—700	12.5	200	-3.2	5c

^a For formation of alk-1-ene [*cf.* Scheme 1; equation (2)] after statistical correction (573 K). In order to eliminate artefacts, data pertain to measurements of AcOBu^t performed by the same author(s) only. ^b *r* = 0.9982. ^c *r* = 0.9990. ^d *r* = 0.9994.

ively, and methylmagnesium iodide. Gas-phase thermolyses were performed with dilute solutions of esters in toluene, using a Pyrex glass microreactor-g.l.c. system, essentially analogous to that described earlier.¹⁶ A few parallel runs were performed in a 'macro' flow system enabling product isolation.¹⁷ For comparison, *t*-butyl acetate was also studied. With all three substrates wall effects were found to be negligible, as a ten-fold increase in surface-to-volume ratio of the reactor had little, if any, effect on the rates. Ester (II) in the temperature region of 538—582 K (residence time 4 s) led to acetic acid and 2,3,3-trimethylbut-1-ene as the only detectable products.* Compound (III) (525—590 K) gave a mixture of the two possible alkenes (Scheme 1), the product ratio being not measurably dependent on temperature.

Discussion

(i) *Steric Acceleration.*—Clearly, an increase in bulkiness of the tertiary alkyl group leads to enhanced rates of elimination. At 573 K, using the Arrhenius parameters in Table 2, relative rates of elimination of AcOH are found to be AcOBu^t : (II) : (III) = 1 : 6.5 : 8.1. When expressed for the formation of the

* This reaction has independently been studied by Chuchani *et al.*^{13a}

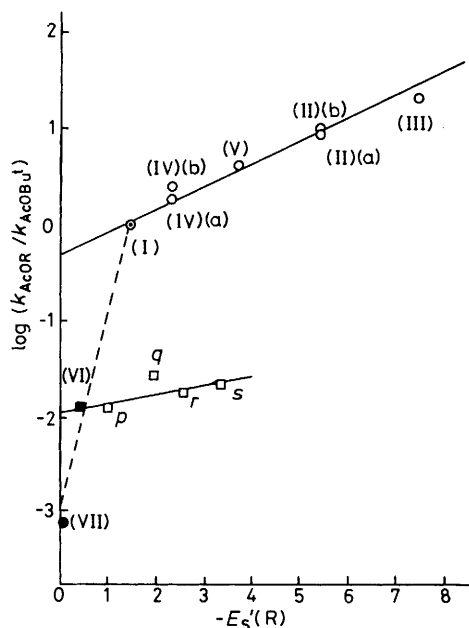


Figure 1. Rates of formation of alk-1-enes from AcOR *versus* the steric parameter ($-E_s'$) for R. Compounds (I)–(VII), see text; compound *p* = AcOCHMeEt; ¹⁸ *q* = AcOCHMe(CH₂Bu^t); ^{13b} *r* = AcOCHMePrⁱ; ^{19a} *s* = AcOCHMeBu^t ^{19b}

alk-1-ene on a per-hydrogen basis these values become 1 : 9.7 : 20.4, corresponding with differences in free energy of activation [AcOBu^t – (II)] 10.9 and [AcOBu^t – (III)] 14.4 kJ mol⁻¹.

In Figure 1 $\log k_{rel}$ ($= \log k_{AcOR}/k_{AcOBu^t}$) for alk-1-ene formation (*cf.* Table 2) is plotted against the steric parameter $-E_s'$ for R.¹⁵ Apart from points for AcOBu^t, (II), and (III) those for AcOCMe₂Et (IV) and AcOCMe₂Prⁱ (V), using reliable literature data, are also included. The five esters constitute a fairly good straight line with slope δ -0.21 (r 0.988). At 573 K this slope corresponds to 2.3 kJ mol⁻¹ per E_s unit. Note that the points for AcOPrⁱ (VI) and AcOEt (VII) are very far off the line for tertiary acetates. Alternatively, one may plot $\log k$ values for tertiary acetates AcOR = AcOCMe₂R' with R' = (H), Me, Et, Prⁱ, and Bu^t *versus* $-E_s'$ for the 'sub'-group R' only. Such a plot turns out to be highly non-linear, however.

The line for representative secondary acetates VI, (*p*–*s*, Figure 1) has a markedly smaller slope of δ -0.09 , equivalent to 1.0 kJ mol⁻¹ per E_s .

$\log k_{rel}$ Values extrapolated to $E_s' \rightarrow 0$ should correspond to strain-free *polar* effects of substitution. These effects amount to $\Delta \log k$ (at 573 K) of 1.1 (Et \rightarrow Prⁱ) and 2.8 (Et \rightarrow Bu^t), or to differences in free energy of activation of *ca.* 12 and 30 kJ mol⁻¹, respectively. These values are commented on later.

The maximum possible relief of strain is that achieved when alkenes are completely formed. As already mentioned in the Introduction, there are no thermodynamic data available for acetates, but a useful approach is to consider (hypothetical) eliminations from corresponding hydrocarbons [equation (1); Y = alkyl rather than OAc]. In Figure 2 heats of reaction (ΔH° , ΔG°) are plotted against $-E_s'(R)$ for 'elimination' of HY (Y = Me, Et, or Prⁱ) from Y-CMe₂R'. The slopes of the corresponding lines are: (a) 3.3, (b) 4.2, and (c) 6.7 kJ mol⁻¹ per E_s' unit. The more strain in the parent molecule, the larger the slope. (Note that the plots include R' = H; in the overall process, alkane \rightarrow alkene + smaller alkane, polar effects appear to be of minor weight.)

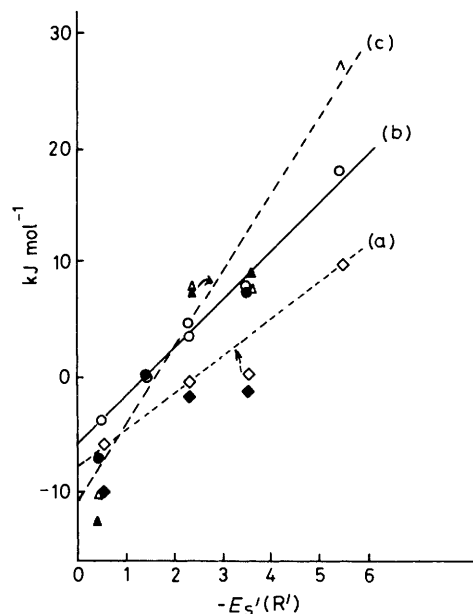


Figure 2. Thermodynamics of 'elimination' from hydrocarbons. $Y-CMe_2R' \rightleftharpoons Y-H + H_2C=CMeR'$ as a function of $-E_s'(R')$. Open symbols, ΔH° , filled symbols ΔG° ; line (a), Y = Me (\diamond , \blacklozenge); (b), Y = Et (\circ , \bullet); (c), Y = Prⁱ (\triangle , \blacktriangle). From left to right: R' = H, Me (reference point), Et, Prⁱ, and Bu^t

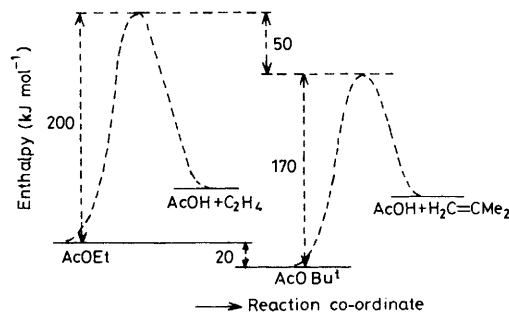


Figure 3. Pyrolysis of AcOBu^t *versus* AcOEt: polar effects of α -alkylation

There is no E_s value available for the acetoxy-group. Judging from data for other oxy-groups,²⁰ the E_s value for AcO cannot possibly be larger than that for Me or Et; *cf.* also 'conformational energies' for cyclohexyl derivatives:²¹ MeO, 2.5; AcO, 3.0; Me or Et, 7.5 kJ mol⁻¹. 'Complete' formation of (primary) alkenes from tertiary alkyl acetates [equation (2)] should therefore have a slope of less than 7, presumably less than 4 kJ mol⁻¹ per E_s . In the transition state for ester pyrolysis only part of the strain present in the starting compound will be relieved. Our experimental values, 1.0–2.3 kJ mol⁻¹ per E_s , constitute a realistic fraction of the 'theoretical maximum' discussed above. In their recent analysis, Martin *et al.*²² have plotted $\log k$ values for AcOCMe₂R' against Taft E_s values for R' = Prⁱ, Me, and hydrogen. The point for R' = Bu^t [our compound (II)] is badly off the line connecting these points, which has a slope of δ *ca.* -1.5 . Likewise, the dotted line connecting the points for AcOBu^t, AcOPrⁱ, and AcOEt in Figure 1 has a slope of δ -2.0 . Such large slopes go far beyond the maximum possible effect for complete elimination as discussed above and therefore have no physical meaning. In other words, the major part of the rate increase AcOEt \rightarrow AcOBu^t must be due to polar rather than to steric effects.

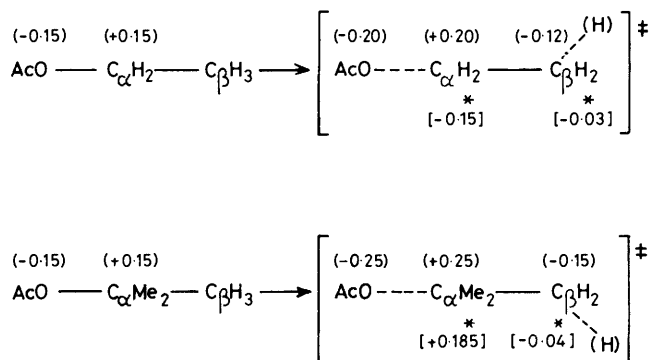
(ii) *Polar Effects of α -Alkylation.*—Knowing that the rate enhancement $\text{AcOEt} \rightarrow \text{AcOBu}^t$ is due virtually entirely to a polar effect, one needs to rationalize the difference in free energy of activation of *ca.* 30 kJ mol⁻¹. To this end the energy diagram of Figure 3 is very helpful. For its proper construction the energy difference between AcOEt and AcOBu^t , the (net) polar effect due to α -alkylation of OEt to give OBu^t , must be known. For this effect a value of 20 kJ mol⁻¹ can be adopted, which is derived as follows.

The strength of the $\text{Bu}^t\text{-H}$ bond is lower than $D(\text{Et-H})$ by 28 kJ mol⁻¹, electronic stabilization of $\text{Bu}^t\cdot$ (ΔH_f° 34) versus $\text{Et}\cdot$ (ΔH_f° 109 kcal mol⁻¹) due to α -alkylation being larger than that in the hydrocarbon. Likewise $D(\text{Et-Y}) - D(\text{Bu}^t\text{-Y})$, with $\text{Y} = \text{Me}$ or primary alkyl, is *ca.* 15 kJ mol⁻¹.^{9,14,*} For compounds $\text{Bu}^t\text{-Y}$ and Et-Y where Y is an electronegative group such as Cl , NO_2 , OR , the carbon-Y bonds are almost equal in strength, however.⁹ This is also expected to hold for $\text{Y} = \text{OAc}$. In the latter cases the bond-weakening effect due to stabilization of $\text{Bu}^t\cdot$ versus $\text{Et}\cdot$ is compensated by electronic (dipolar) stabilization in $\text{Bu}^t\text{-Y}$ compared with Et-Y . In order to establish the magnitude of this effect one can choose $\text{Y} = \text{H}$ or $\text{Y} = \text{primary alkyl}$ as a reference, so as to obtain 28 or 15 kJ mol⁻¹, respectively. A round figure of 20 kJ mol⁻¹ is fully adequate for the present discussion. When setting the difference in height of the two activation barriers at 30 kJ mol⁻¹ (Figure 3),† it is seen that the energy level of $[\text{AcOBu}^t]^\ddagger$ is *ca.* 50 kJ mol⁻¹ below that of $[\text{AcOEt}]^\ddagger$.

The corresponding net effect of α -alkylation for gaseous ions, $\text{Et}^+ - \text{Bu}^{t+}$, is *ca.* 170 kJ mol⁻¹, *viz.* 150 (the difference in ionization energy, see Introduction) plus 20, the effect in the starting esters. Hence, the polar stabilization of *ca.* 50 kJ mol⁻¹ of the transition state for β -elimination is nearly one-third of that for full ionization, suggesting the development of an elementary charge no less than 0.3 on α -carbon in $[\text{AcOBu}^t]^\ddagger$. How can this be reconciled with the very modest Hammett ρ values quoted above?

For a proper answer the following aspects are important. (1) In the starting compounds there is already a positive charge present at α -carbon. The overall dipole moments of AcOEt and AcOBu^t (in apolar solvents) are nearly the same, 1.8–1.9 D.²³ Translation of this value into point charges $\delta(+, -)$ at bonding distance (*ca.* 150 pm) *via* the relationship $\mu = 4.8 \text{ e.r.}^{24}$ yields δ *ca.* 0.25 atomic units. This is very probably an overestimation for the partial dipole moment associated with the O-C_α bond. Another approach is to compare the net energy difference between AcOEt and AcOBu^t of 20 kJ mol⁻¹ (Figure 3) with that for full ionization (170 kJ mol⁻¹). Assuming charges on α -C in AcOEt and AcOBu^t to be the same (*cf.* dipole moments), one arrives at δ 0.12 atomic units. We will adopt the value δ 0.15 further on.

(2) When going to the transition state δ^+ on C_α increases, but this increase is larger for AcOBu^t than for AcOEt , as can be inferred from the Hammett ρ values for the corresponding series of benzoates, 0.26 and 0.58, respectively.⁵ Simultaneously a negative charge develops at C_β which, according to Taylor, amounts to *ca.* 60% of δ^+ on C_α . This has consequences for the magnitude of substituent effects at C_α and at C_β . In series such as $\text{AcOCH}(\text{Me})\text{C}_6\text{H}_4\text{Z}$ the *effective* positive charge experienced by $\text{C}_6\text{H}_4\text{Z}$ on C_α , therefore, is *ca.* $60/2.3 \approx 25\%$



Scheme 2.

less than the actual δ^+ value, due to the 'inductive fall-off factor' of *ca.* 2.3 per C-C bond.^{5a} Likewise, the 'net' negative charge experienced by substituents at C_β in *e.g.* $\text{AcOCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Z}$ will be less than one-third of the 'real' value,^{5a} in line with typical experimental ρ values of *ca.* -0.6 (C_α) and +0.2 (C_β), respectively.^{2c}

If we neglect possible differences in potential energy associated with other regions of the two six-membered transition states, a model of charge distributions such as that given in Scheme 2 offers a rationale for the seemingly contradictory rate data on α -alkylation and from Hammett studies (numbers given an asterisk denote effective charges as outlined above). For example, the increase in negative charge of the acetoxy-group is twice as large (0.10 units) for AcOBu^t as for AcOEt (0.05 units). Furthermore, the *effective* increase in positive charge on C_α of AcOBu^t is a few hundredths only (*viz.* from 0.15 to 0.185), as demanded by the low ρ values observed for benzylic acetates.^{5b}

A (net) positive charge at C_α of $[\text{AcOBu}^t]^\ddagger$ of 0.25 or less, stabilized by three methyl groups, is not enough to cover the energy difference of *ca.* 50 kJ mol⁻¹ between the two transition states, as it accounts for at best $0.25 \times 170 \approx 40$ kJ mol⁻¹. However, the electrostatic interaction *per se* between the incipient charges on C_α and C_β will also play a part. The C_βH_3 group, about to lose hydrogen and carrying a negative charge in the transition state, is a substituent at C_α with much better stabilizing abilities than 'ordinary' methyl groups. The magnitude of this stabilization is larger in $[\text{AcOBu}^t]^\ddagger$ than in $[\text{AcOEt}]^\ddagger$. A rough estimate of the energies involved can be made as follows. As two unit charges at a distance of 150 pm involve a potential energy of *ca.* 800 kJ mol⁻¹, the Coulomb energies associated with the dipoles $\text{C}_\alpha\text{-C}_\beta$ in Scheme 2 are calculated to be 20 for $[\text{AcOEt}]^\ddagger$ and *ca.* 30 kJ mol⁻¹ for $[\text{AcOBu}^t]^\ddagger$. The difference of *ca.* 10 kJ mol⁻¹ is about the amount of energy we were still 'missing'.

Having sorted out steric and polar effects and after having discussed both effects in a (semi-)quantitative way, the effect of substituents at C_α other than alkyl can now be analysed properly. This will be done in a subsequent paper.²⁵

Experimental

Apparatus.—The g.l.c. microreactor system used is a modernized version of that described earlier;¹⁶ gas flows in the reactor and g.l.c. column can be independently established. A Pyrex glass reactor *a* (see Figure 4) of requisite dimension (from tubular to bulb-shaped) and with an effective length (heated part) of *ca.* 12 cm, is connected to a movable standard g.l.c. injection block *b* (Becker Delft) and, *via* a balljoint, to a splitter *c*, which in turn is connected to a standard g.l.c.

* Conversion of Et-R into $\text{Bu}^t\text{-R}$, having a fully alkylated carbon atom, is 13 kJ mol⁻¹ more favourable than α -alkylation of Et-H to give $\text{Bu}^t\text{-H}$: the more branching, the higher the stability of alkanes.

† The two barriers are drawn to be 200 and 170 kJ mol⁻¹, in line with experiment (Table 2). The use of ΔG^\ddagger rather than ΔH^\ddagger values would have little influence on the discussion of the polar effect, as $\log A$ values for the two esters, after statistical correction, differ by 0.3 only.^{5c}

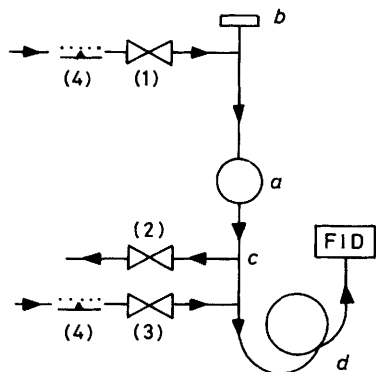


Figure 4.

apparatus *d* (Hewlett-Packard 5701; DMCS column). The flow (and hence residence time) in *a* is regulated by a Porter constant-flow valve (1), the fraction of the pyrolysate entering the column of *d* is governed by an Inacom needle valve (2). The described total flow through *d* can be arranged *via* the standard HP gas inlet system (3). Gas streams are measured *via* HP flowmeters (4) and a soap-film meter connected to (2). Reactor *a* is heated by a home-made electric cylindrical oven (height 12 cm, 1 000 W, 220 V, maximum temperature 700 °C), constructed in two halves enabling easy replacement of reactors and also rapid cooling, if desired. Temperatures are set using Honeywell Versapak II proportional controllers and checked *via* a chromel–alumel thermocouple and a Philips microvoltmeter (accuracy better than 1° at 0–500 °C).

Typical residence times are from 1–8 s. In the present investigation we have used a tubular reactor, inner diameter *ca.* 0.3 cm, effective volume *ca.* 0.72 ml, surface-to-volume ratio *ca.* 14. With a flow rate of nitrogen through (1) of nearly 11 ml min⁻¹ (at the appropriate temperature) the residence time is 4.0 s. Usually, the flow of nitrogen through *d* was 25 ml min⁻¹. The 'macro' tankflow-type reactor system used is described elsewhere.¹⁷

1,1,2,2-Tetramethylpropyl Acetate (II).—The carbinol (hydrate) was made from Bu^tC(O)Me and MeMgI in ether (0.5 mol each), yield 95%, m.p. 80 °C (lit.,²⁶ 80 °C). The carbinol (12 g, 0.09 mol) was dissolved in dry ether, a little toluene-*p*-sulphonic acid was added, and ketene (0.2 mol h⁻¹, made by cracking acetone) was passed through ^{7b} for 3 h. After standing overnight g.l.c. analysis indicated *ca.* 90% conversion into acetate. After evaporation of solvent, fractional distillation afforded (II) (6.4 g, 44%), b.p. 75 °C at 50 mmHg, δ_{H} (CCl₄) 1.0 (s, Bu^t), 1.5 [s, -C(CH₃)₂], and 2.0 (s, OCOCH₃). G.l.c. analysis showed the material to be of >99% purity.

1-Isopropyl-1,2-dimethylpropyl Acetate (III).—The carbinol was made from Prⁱ₂C=O and MeMgI (0.6 mol each), yield 84%, b.p. 70 °C at 33 mmHg (lit.,²⁷ b.p. 101 °C at 125 mmHg). Carbinol (13 g, 0.1 mol) was treated with ketene (see above, but the rate was much lower). After 6 h, conversion was *ca.* 10%. By preparative g.l.c. (Varian; 150 °C) a fraction of (III) contaminated with *ca.* 30% of the carbinol was isolated. As the alcohol turned out to be thermally stable when pyrolysing (III), this mixture was used as such, employing the alcohol as internal standard for g.l.c. analysis, δ_{H} (CCl₄) 0.85 [2d, (CH₃)₂C], 1.28 [s, AcOC(CH₃)], 1.80 (s, OCOCH₃), and 2.20 (m, 2 × CMe₂H).

2,3,3-Trimethylbut-1-ene.—This pyrolysis product of (II)

was made from the carbinol and 70% sulphuric acid,²⁸ δ_{H} (CCl₄) 1.00 (s, Bu^t), 1.65 (s, CH₃), and 4.63 (d, H₂C=).

2-Isopropyl-3-methylbut-1-ene and 2,3,4-Trimethylpent-2-ene.—These are products from (III) (*cf.* Scheme 1) and were independently made from the carbinol and I₂.²⁹ Work-up resulted in a 1 : 2 mixture as described,²⁹ whereas pyrolysis of (III) gave a *ca.* 5 : 1 ratio. Both mixtures had identical g.l.c. retention times.

Pyrolyses.—Acetates were pyrolysed using 5% w/w solutions in toluene. Rates measured in the macroreactor system, with a low surface-to-volume ratio of *ca.* 1,¹⁷ tallied well with those obtained with the tubular microreactor (*s* : *v* ratio *ca.* 14). Hence, wall effects were unimportant, in line with earlier experience with tertiary acetates.³ Ester conversions and/or amounts of alkenes formed were determined by g.l.c.; macro runs enabled also titration of acetic acid formed. Kinetic data are summarized in Table 1.

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