The Mechanism of Thermal Elimination. Part 17.[1] Rate Data for Pyrolysis of Vinyl Acetate and 1,2-Diacetoxyethane

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Between 721.7 and 636.4 K, vinyl acetate undergoes thermal decomposition according to the rate equation $\log (k/s^{-1}) = 10.43 - 182.4/2.303 \ RT$ (R = 8.312 J mol^{-1} K^{-1}). Approximately 95% of reaction is decarbonylation to give acetone, with decomposition to ketene and acetaldehyde being the minor component. The latter reaction is an analogue of acetic anhydride pyrolysis which takes place at least 10^6 times faster per β-hydrogen at 600 K. This very large rate difference parallels that between β-keto-acids and βγ-alkenoic acids and contrasts markedly with pyrolysis of alkyl acetates and alkyl vinyl ethers, which occurs at closely similar rates. The contrasting behaviour most probably reflects differences in the principal bond-breaking step of the reaction, which for vinyl acetate and acetic anhydride (and also the acids) is breaking of the β-X-H bond so that the nucleophilicity of the attacking group assumes major importance; for esters and vinyl ethers this is not the most important step so their reaction rates are similar. The relative reactivities to the acids support an alternative view that both vinyl acetate and acetic anhydride pyrolyse *via* their enol forms. The greater understanding of the factors affecting gas-phase elimination rates permits prediction of the relative rates of compounds not yet studied. Pyrolysis of 1,2-diacetoxyethane gave non-first-order plots, with rate acceleration due to formation of the more reactive vinyl acetate. The β-acetoxy-group (OCOMe) increased the rate of elimination (per β-hydrogen at 600 K) *ca.* 7-fold, which compares with factors of 388 and 144 for COMe and CO$_2$Me respectively, and a reduction of 3.6-fold by OMe.

This series of papers is aimed at accurately quantifying the factors which produce changes of rate in gas-phase six-centre eliminations (I). One feature of interest is what happens when the group F is changed. An initial assumption might reasonably be that making F more nucleophilic would produce an increase in rate, and thus, for example, thionacetates (F=S) are more reactive than acetates (F=O).[2] However, this would be an oversimplification, because for a given pair of groups F the reactivity order can invert according to the nature of the other components constituting the six-membered ring (see Discussion). In this connexion we were interested in the relative rates of elimination of acetic anhydride (II) and vinyl acetate (III), the main difference between them being the nature of the nucleophilic group F.

Acetic anhydride undergoes elimination very readily,[3] whereas vinyl acetate was reported[4] to be virtually stable at 420 °C. This latter seemed to us to be improbable and might, for example, have been due to a very short residence time in the flow apparatus used. Nevertheless, this report indicated that vinyl acetate must be fairly unreactive relative to acetic anhydride and at first sight this seems curious in view of the fact that esters, *e.g.* (IV) and vinyl ethers, *e.g.* (V) have closely similar elimination rates;[5,6] we therefore undertook a kinetic study of the elimination.

Allen *et al.* found that at 500 °C vinyl acetate decomposes by four routes.[4] In current terminology, two of these [(1) and (2)] are E_i eliminations, (the mechanisms were incorrectly postulated[4] as four-centre processes), one (3) is an S_Ni reaction, and (4) is an S_Ni reaction followed by elimination; formation of the intermediate ketoaldehyde in the latter process was also incorrectly shown as proceeding through an ionic transition state inapplicable to the gas-phase. Of these reactions, (2) and (4) were shown to be the most important and accounted for *ca.* 95% of the total, with (4) (determined from analysis of acetone and carbon monoxide in the product) comprising at least 50% of this, the amount depending upon conditions.

(I)

(II) (III) (IV) (V)
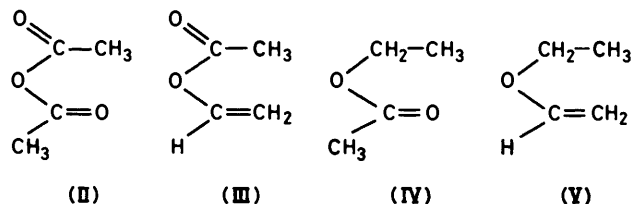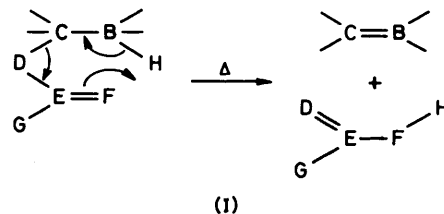
Results and Discussion

Vinyl acetate was pyrolysed over the temperature range 636.4—721.7 K, and the kinetic data are given in Table 1. At the highest elimination temperature the products were trapped in dry ice–acetone and examined by n.m.r., which showed the presence of acetone [from reaction (4)] and acetaldehyde [from reaction (2)] in the ratio of *ca.* 20 : 1; ketene and a trace (<1%) of unreacted vinyl acetate were detected. The reaction stoicheiometry was *ca.* 2.2 at 10 × $t_{\frac{1}{2}}$, being greater than the theoretical value of 2.0, owing to the well known decomposition of acetone and acetaldehyde.[7] The relatively small difference between the observed and calculated values rules out the possibility that reaction (2) is a major one with little acetaldehyde being detected in the products because of its subsequent decomposition.

Because of the secondary decomposition, the kinetic plots of $\log (P_\alpha - P_0)$ *versus* time were only linear to *ca.* 40% of
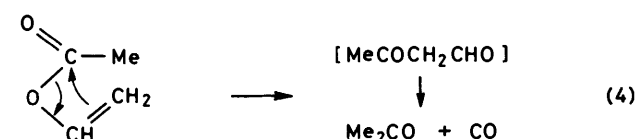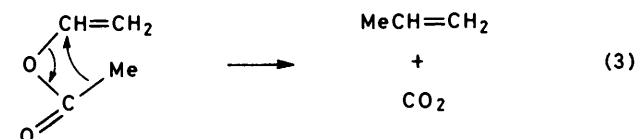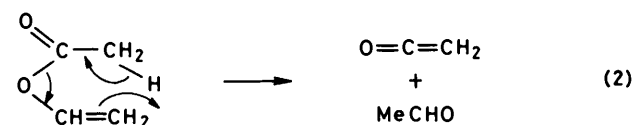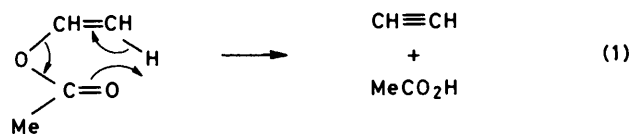
$$\text{(structure: CH=CH, O, C=O, Me)} \longrightarrow CH\equiv CH + MeCO_2H \quad (1)$$

$$\text{(structure: O=C, O, CH=CH}_2\text{, CH}_2\text{)} \longrightarrow O=C=CH_2 + MeCHO \quad (2)$$

$$\text{(structure: CH=CH}_2\text{, O, Me, C, O)} \longrightarrow MeCH=CH_2 + CO_2 \quad (3)$$

$$\text{(structure: O=C, Me, O, CH}_2\text{, CH)} \longrightarrow [MeCOCH_2CHO] \longrightarrow Me_2CO + CO \quad (4)$$

Figure. Arrhenius plot for pyrolysis of vinyl acetate

Table 1. Pyrolysis of vinyl acetate

T/K	$10^3 k/s^{-1}$	$\log (A/s^{-1})$	$E/kJ\ mol^{-1}$	Correlation coefficient
636.4	0.0285	10.43	182.4	0.999 64
666.4	0.140			
682.6	0.282			
688.8	0.376			
690.5	0.404			
696.4	0.573			
708.9	0.990			
721.7	1.70			

reaction if the observed P_∞ was used. However, by extrapolating the pressure increase for the secondary reaction back to time zero, the P_∞ value for the secondary reaction could be determined. (This is the standard procedure in the event of substantial secondary decomposition.) Using this new value of P_∞ good linear plots to >80% of reaction were obtained, and the kinetic data are assembled in Table 1 and also plotted in the Figure. We note the following points.

(i) Two reactions, (2) and (4), are occurring and in contrast to the previous study (at 100 °C higher) we find reaction (4) to be dominant. These results collectively indicate that reaction (2) has the higher activation energy (and must therefore have the higher log A value). Furthermore one could expect the Arrhenius plot to show curvature (concave upwards) and, indeed, inspection of the Figure reveals this, although it is slight. It would have been valuable to have been able to examine the reaction at higher temperatures to show this curvature more clearly, but unfortunately our present apparatus cannot be used at temperatures significantly above those employed in this study.

(ii) Since both reactions occur simultaneously, the Arrhenius values are composite ones, but must be approximately correct fo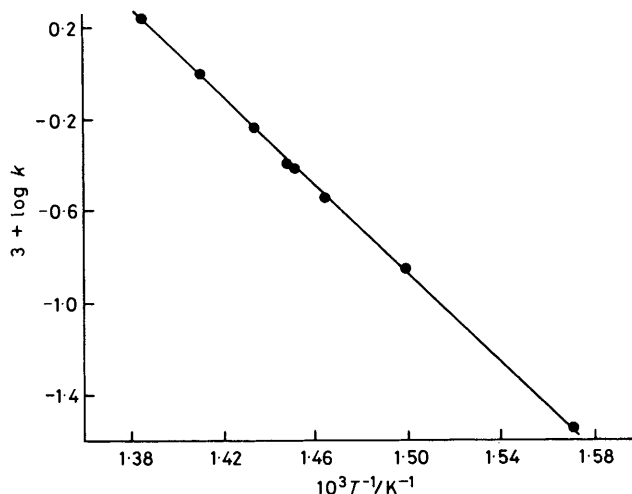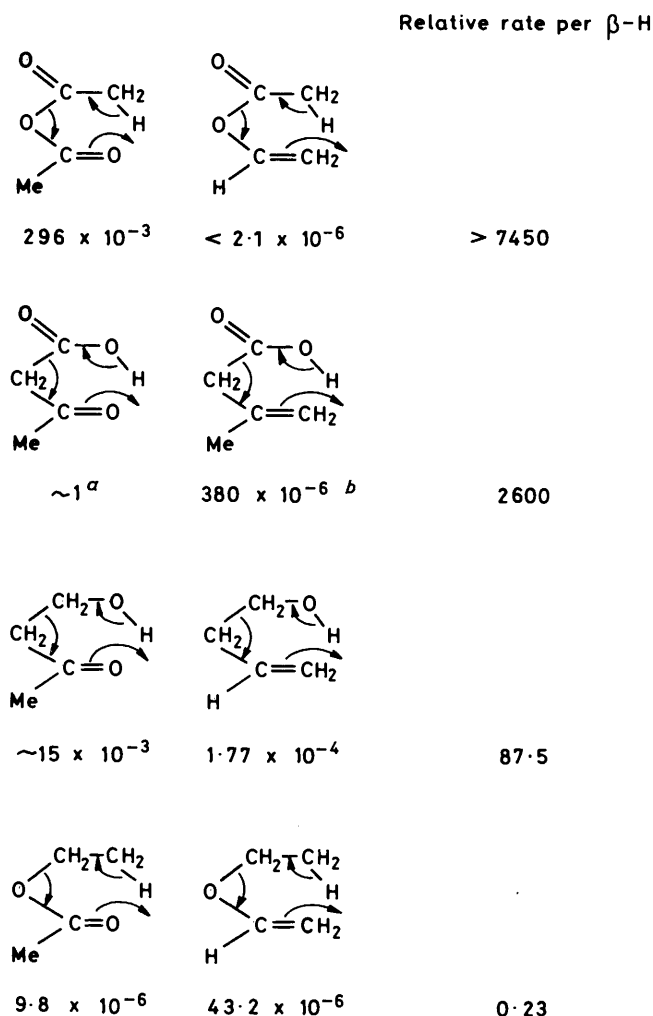r the predominant reaction (4). The log A value is rather low for a cyclic elimination but probably reflects the fact that the overall reaction (4) is two step.

(iii) Vinyl acetate is, as we expected, rather less stable than indicated by the preliminary study.[4] From the Arrhenius data we may calculate the rate coefficient for elimination at 600 K as 2.12×10^{-6} s^{-1}. We show this in the Scheme as deriving entirely from reaction (2), though the true value for this reaction is probably about 10-fold less. This reaction is then *at least* 7 500 times slower per β-hydrogen than the comparable reaction of acetic anhydride. The large rate difference between these compounds parallels that between βγ-alkenoic acids[8] and β-ketoacids,[9] and that between β-hydroxyalkenes[10] and β-hydroxyketones,[11] but contrasts with the closely similar reactivities of vinyl ethers[5] and acetates[6] (see Scheme). For these last two classes of compounds the $C_\alpha-O$ bond is polar and breaking of this is the principle rate-determining step of the reaction. In comparison, breaking of the β-X-H (in this case C-H) bond is relatively unimportant so that the difference in basicity of the C=O and C=CH$_2$ group does not significantly affect the rate.

For the former classes of compounds, the bond to the C_α carbon is not very polar so that breaking of this bond is now not an important contributor to the overall rate. By contrast, the β-X-H bond (in the case of the acids, hydroxyketones, and hydroxyalkenes this is the β-O-H bond) is very polar and breaking of this is principally rate-determining leading to a much greater rate when the attacking base is C=O rather than C=CH$_2$. A similar difference in rate is found for acetic anhydride *versus* vinyl acetate and this clearly indicates that the most important step here also is attack by these basic groups upon the β-X-H bond. We may not be certain however that attack is upon the β-C-H bond because there are good grounds for believing that acetic anhydride pyrolyses *via* the enol form[12] in which case vinyl acetate should do likewise; the similarities of the relative reactivities of the first two sets of compounds in the Scheme would seem to support this view.

(iv) It is appropriate to consider why reaction (1) does not take place very readily. The lack of free rotation about the $C_\alpha-C_\beta$ bond should aid elimination, and probably more than compensate for the fact that there is only one β-hydrogen available for elimination. The sp^2 hybridisation of both α- and β-carbons should aid β-C-H bond breaking but hinder α-C-O bond breaking (and to a greater extent since the latter would for this elimination be more rate determining). How-

Relative rate per β-H

296 × 10⁻³   < 2·1 × 10⁻⁶   > 7450

~1 ^{a} 380 × 10⁻⁶ ^{b} 2600

~15 × 10⁻³   1·77 × 10⁻⁴   87·5

9·8 × 10⁻⁶   43·2 × 10⁻⁶   0·23

Scheme. Rate coefficients k/s^{-1} for elimination at 600 K

^{a} This compound and β-ketoacids in general decompose fairly rapidly in boiling water.[9] The rate is estimated from an assumed log (A/s^{-1}) of 12.0 and hence $E_a = 122$ kJ mol⁻¹, and an acceleration of the reaction in water due to solvation of *ca.* 20—30 fold. (Polar solvents cause comparable acceleration of other cyclic eliminations.[13]) ^{b} Based on the literature data.[8]

(VI)
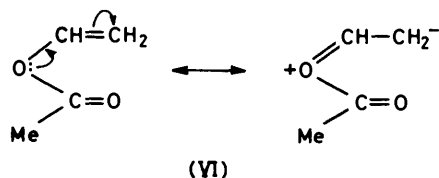
ever, it is likely that the most important feature is the resonance (VI), which increases the strength of the C_α–O bond which has to be broken in the transition state. (This will also reduce the usual resonance between the ethereal oxygen and the carbonyl group that takes place in esters, thereby reducing the basicity of the carbonyl group.)

(v) In view of the low reactivity of vinyl acetate, it would be expected that phenyl acetate (VII), in which the double bond is delocalised into the aromatic ring, would be substantially less reactive. This we confirmed, runs carried out at 660 K showed no significant elimination, and this is also consistent
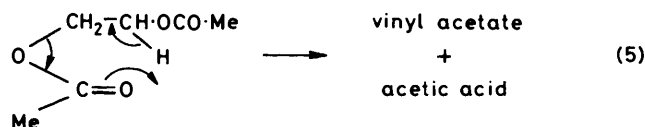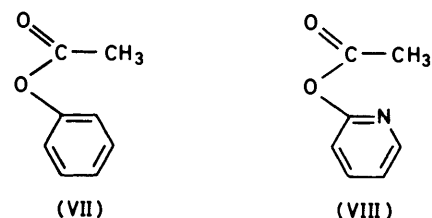

(VII)   (VIII)

$$\longrightarrow \quad \text{vinyl acetate} + \text{acetic acid} \quad (5)$$

Table 2. Accelerating effects per β-H at 600 K of β-substituents

Substituent	Effect	Electronic type	Reference
OMe	0.28	$-I, +M$	14
COMe	388	$-I$, strong $-M$	15
CO₂Me	144	$-I, -M$	16

with the low reactivity towards elimination of 2-pyridyl acetate (VIII),[13] which has a more basic attacking group than in phenyl acetate.

Pyrolysis of 1,2-*Diacetoxyethane* [*Reaction* (5)].—This was undertaken in order to determine the effect of the β-acetoxy-group on the rate of elimination, a factor of some importance in assessing the cause of instability of certain polymers. Previously the effects of the β-OMe, COMe, and CO₂Me groups have been determined (Table 2) and from these results the effect of the OCOMe substituent could be expected to lie between that of OMe and COMe.

Accurate rate data could not be obtained because rate acceleration occurred during the runs due to the subsequent more rapid elimination of the first formed vinyl acetate. Very approximate rate data for equation (5) were obtained at 682.6 and 690.5 K as 2.4 × 10⁻⁴ and 3.6 × 10⁻⁴ s⁻¹, respectively, so that the corresponding rate coefficients per β-hydrogen were 0.6 × 10⁻⁴ and 0.9 × 10⁻⁴ s⁻¹. Comparison with the values that may be calculated from the Arrhenius data for ethyl acetate[6] shows that the β-acetoxy-group accelerates elimination *ca.* 7-fold, which is thus between the effects of OMe and COMe, as expected.

Experimental

Commercial vinyl acetate was fractionally distilled to remove the stabilizer, and 1,2-diacetoxyethane was prepared from ethylene glycol in the usual way.

The static kinetic procedure using a stainless-steel reactor has been described previously in detail.[17] For vinyl acetate, rate coefficients were reproducible to ±2% and no more than two runs were required at any temperature to achieve this reproducibility. This is consistent with our observation over many years that unreactive compounds are the least sensitive to surface catalysis. A 4-fold variation in the amount of compound taken for a run (50—200 μl) gave no variation in rate coefficient outside the reproducibility value noted above, and these observations taken together indicate the absence of reactions involving radical processes.

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