The Mechanisms of Thermal Eliminations. Part 12.[1] Relative Rates of Pyrolysis of Ethyl, Isopropyl, t-Butyl, and n-Butyl Vinyl Ethers: Rate Spread as an Index of Elimination Mechanisms

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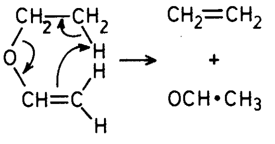
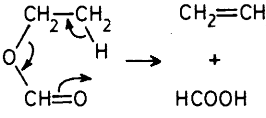
Rate coefficients have been measured between 594.5 and 681.0 K for pyrolysis of ethyl, isopropy, t-butyl, and n-butyl vinyl ethers. The relative rates of elimination at 600 K are: 1.0, 10.0, 178, and 1.52, the Arrhenius data [E/kJ mol^{-1}, log (A/s^{-1})] being: ethyl, 185.92, 11.826; isopropyl, 182.51, 12.527; t-butyl, 164.05, 12.169; n-butyl, 177.64, 11.284. These results show that the literature data for t-butyl vinyl ether elimination are considerably in error, confirming the prediction based on statistical mechanics. The relative primary, secondary, and tertiary elimination rates are consistent with those obtained from a range of thermal eliminations, whereas the relative rates based on the literature data are not. Analysis of the relative primary, secondary, and tertiary elimination rates from this and other reactions permits prediction of rates for secondary and tertiary compounds as yet unmeasured, and also suggests that some literature data may be in error through the incursion of side reactions. A β-ethyl group increases the rate of elimination 2,3-fold per β-hydrogen at 600 K (*cf.* 1.62 for acetates) and may likewise be due to steric acceleration, though the possibility of electron acceptance by alkyl groups in the gas-phase cannot be excluded. The product distribution in pyrolysis of 1-methylpropylvinyl ether is shown to be accounted for by the nature of the transition state. Vinyl ethers do not pyrolyse 50° below the corresponding esters as recently claimed. Tertiary vinyl ethers are for example less reactive than tertiary esters.

THIS series is directed towards providing very accurate rate data for a range of compounds which undergo thermal elimination *via* a six-centred transition state, and thus to be able to quantify the factors which produce changes in rate. For this it is necessary to accumulate a large body of rate data, all obtained under precisely the same conditions. Comparisons of literature data are unsatisfactory because of the discrepancy between real and measured temperatures (arising from thermocouple errors and reaction vessel end effects) and in some studies, the incursion of surface-catalysed reactions.

In this paper we describe pyrolysis of vinyl ethers, *e.g.* ethyl vinyl ether (I) which decomposes *via* a cyclic transition state analogous to that which applies to esters, *e.g.* ethyl formate (II).



(I)



(II)

The pyrolysis of ethyl vinyl ether was first studied kinetically by Wang and Winkler[2] who showed that the primary process was decomposition into ethylene and acetaldehyde, though they incorrectly described the process as four- rather than six-centre as in (I). They showed that the reaction was accompanied by some secondary decomposition of acetaldehyde, but this did not seriously interfere with the determination of the rate coefficients leading to the Arrhenius data given in Table 1. A subsequent determination by Blades and Murphy[3] gave closely similar values, and Blades also measured the rate for the isopropyl compound,[4] as did Bamkole and Emovon[5] (see Table 1). Significantly, these latter workers obtained somewhat lower E_a and log A values and their kinetic study of t-butyl vinyl ether (pyrolysis of which rules out the four-centre mechanism of Wang and Winkler) showed anomalously low values for both parameters. The doubtful validity of these results has been noted by Richardson and O'Neal[6] who calculated by statistical mechanics, values of 40.4 kcal mol^{-1} and 12.4 s^{-1}. They suggested that Bamkole and Emovon were studying a reaction with a substantial free-radical chain sensitized component. This would be surface catalysed, but Bamkole and Emovon concluded that their results were free of any surface effects because ' a five-fold increase in the surface to volume ratio of the vessel did not alter the rates outside experimental error.' We have for some time considered this generally accepted evidence for the absence of surface catalysis to be of minimal value, because one cannot be certain that the pressure of initial reagent has been reduced to the point where the ratio of heterogeneous to homogeneous reaction becomes large enough to make a detectable variation in the rates, especially if the surface catalysis is not large. A more sensitive test in our experience is the absence of deviant points on the Arrhenius plot coupled with reasonable log A values. It is our experience that the more reactive compounds in a series of like structure are more prone to

TABLE 1

Arrhenius data for pyrolysis of alkyl vinyl ethers ROCH=CH_2

R	log (A/s^{-1})	E/kcal mol^{-1}	10^3k/s^{-1} at 600 K	Ref.
Ethyl	11.602	44.40	0.0267	2
Ethyl	11.431	43.80	0.0298	3
Ethyl	11.826	44.436	0.0432	This work
Isopropyl	12.58	43.56	0.514	4
Isopropyl	12.12	42.56	0.412	5
Isopropyl	12.527	43.621	0.432	This work
t-Butyl	10.86	36.184	4.76	5
t-Butyl	12.169	39.209	7.68	This work

surface catalysis which manifests itself in a low E_a and hence a low log A value which will be lower than for a less reactive member of the series. This would mean that at some temperature the compounds change their relative reactivities, a nonsense in our view. Thus we regard abnormally low log A values as a guarantee of surface catalysis, and therefore considered it appropriate to re-examine the pyrolysis of the t-butyl vinyl ether.

TABLE 2

Pyrolysis of compounds ROCH=CH$_2$

R	T/K	10^3k/s^{-1}	log (A/s^{-1})	E/kJ mol^{-1}	Correlation coefficient	log k at 600 K
Ethyl	617.1	0.116	11.823	185.92	0.998 87	−4.3649
	638.1	0.437				
	649.7	0.741				
	661.7	1.43				
	677.4	2.97				
Isopropyl	617.1	1.19	12.527	182.57	0.998 38	−3.3645
	638.1	3.87				
	651.0	7.37				
	661.7	12.6				
	677.4	26.5				
t-Butyl	594.5	5.75	12.169	164.05	0.998 37	−2.1147
	608.2	11.9				
	617.1	20.2				
	638.1	58.3				
	651.0	95.5				
n-Butyl[a]	649.7	0.999	11.284	177.64		−4.1834
	681.0	4.45				

[a] Literature values [14] are E/kJ mol^{-1} 177.33 and log (A/s^{-1}) 11.152.

The problem with determining relative rates from the literature data of different workers and techniques is evident from the published data in Table 1. These give Pr^i/Et rate ratios between 13.8 and 19.3 and relative Bu^t/Pr^i rate ratios between 9.3 and 11.5 (at 600 K). The variation in the former value and the fact that the latter ratio is *smaller* than the former (improbable if the C$_\alpha$–O bond is significantly polarised in the transition state), made necessary the re-examination of the pyrolysis of all three compounds.

RESULTS AND DISCUSSION

Each compound gave good first-order kinetics to at least *ca.* 85% of reaction. At the calculated P_∞ the pressure continued to rise slightly due to the secondary decomposition of the acetaldehyde and this became less important along the series primary > secondary > tertiary, as expected. Correction of P_∞ for this secondary decomposition then gave kinetics with at least 95% linearity and first-order rate coefficients which were reproducible to better than ±2%. The rate coefficients were obtained over at least 55° for ethyl, isopropyl, and t-butyl vinyl ethers, and the average values determined at each temperature are given in Table 2 along with the derived Arrhenius data.

Comparison with Previous Arrhenius Data.—The Arrhenius data are gathered in Table 1 along with those previously determined. Our results for ethyl vinyl ether agree very closely with the original study by Wang and Winkler,[2] and it appears that the results of Blades and Murphy [3] may have been very slightly affected by a surface component. Our results for the isopropyl compound are virtually identical to those of Blades [4] thereby confirming our belief that the studies of Bamkole and Emovon were affected by surface catalysis. This view is reinforced by our data for t-butyl vinyl ether which give much higher values than they obtained, and indeed our results are close to those predicted theoretically.[6]

The Arrhenius data are compared to those for the corresponding acetates in Table 3 from which it is clear that the vinyl ethers generally give lower E_a and log A values. This latter may reflect the intrusion of seven atoms in the six-membered transition state for vinyl ether pyrolysis (I), *i.e.* this transition state is sterically less favourable than that for acetates (II). Another interesting feature is the generally larger log A values for pyrolysis of the secondary and tertiary vinyl ethers, compared with the primary compound. This was also true for pyrolysis of various classes of esters,[7] and also of alkoxypyridines,[1] and we attribute it to the statistical effect of the greater number of β-hydrogens. If this is correct then the difference in the log A values for the primary, secondary, and tertiary compounds should ideally be the logarithms of the ratios of the number of β-hydrogens, *i.e.* log A (Pr^i − Et) 0.301 and log A (Bu^t − Pr^i) 0.176.

TABLE 3

Arrhenius parameters for pyrolysis of acetates [7] and vinyl ethers

		Ethyl	Isopropyl	t-Butyl
E/kJ mol^{-1}	Acetate	201.04	192.25	169.90
	Vinyl ether	185.92	182.51	164.05
δ E		15.12	9.74	5.55
log (A/s^{-1})	Acetate	12.496	13.190	13.279
	Vinyl ether	11.826	12.527	12.169
δ log A		0.673	0.663	1.110

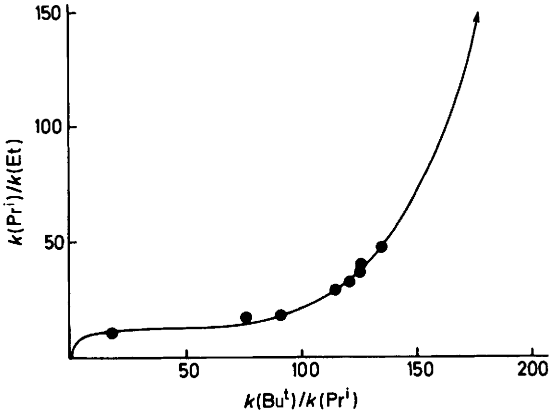
Polarity of the Transition State.—The Et/Pr^i/Bu^t rate ratio at 600 K is 1 : 10.0 : 178 so that the Pr^i/Bu^t ratio is 17.8 and both these are substantially different from those which could be calculated from the literature results (see Introduction). The rate spread shows that vinyl ether pyrolysis is a less polar reaction than for many other gas-phase eliminations (Table 4) which follows from the low polarity of the C=CH_2 bond. The data in Table 4 are also displayed in the Figure, the shape of which can be rationalised as follows. For a very non-polar reaction, *i.e.* one with little charge developing at the α-carbon, the differential electron-supplying effects of alkyl groups on stabilizing this charge will be insignificant. Therefore the relative reaction rates will be governed only by the statistical effect of the number of β-hydrogens, *i.e.* the Pr^i/Et and Bu^t/Pr^i rate ratios will be *ca.* 2.0 and 1.5, respectively. As we go to a potentially more polar reaction, initially only the polarity of the transition states for the t-butyl compound will increase, leading to a large increase in the Bu^t/Pr^i rate ratio. As the opportunity for charge separation increases, eventually the polarity of the transition states for the isopropyl compounds will begin to increase and this will appear as an increase in the Pr^i/Et rate ratio. Since the amount of polarity in the transition state for a gas-phase reaction is very limited, the polarity of the transition states for t-butyl compounds will approach this limit, and the Pr^i/Et ratio will catch up on the Bu^t/Pr^i ratio (as in halide pyrolysis). For the most polar reactions the point should be reached where these ratios become again governed only by statistical effects as in very non-polar reactions. The arguments extend those which one of us has given previously.[7,11] From the Figure it should be possible to predict the ratios for reactions where they have not been measured, provided two of the three ratios are known, *e.g.* the Pr^i/Et and Bu^t/Pr^i values are predicted to be 17 and 85, respectively, for thionacetates, and 11 and 20 respectively for dithioacetates, based on the overall Bu^t/Et ratio,[12] calculated at 600 K to be 1 475 and 213, respectively. For trifluoroacetates Blake and Shraydeh [10] have very recently found a Pr^i/Et ratio of 47, so that from the Figure a Bu^t/Pr^i value of 135 is predicted and the rate coefficient for the homogeneous elimination of the t-butyl ester may be calculated at 600 K to be $817 \times 10^{-3}\ s^{-1}$. We are very confident in this value because if we assume a log *A* value of 12.7 s^{-1} (the same as the isopropyl compound, which is approximately true for all esters [7]) then E_a is 35.1 kcal mol^{-1}, precisely the value predicted by comparison with other ester types.[10] Kinetic studies on the t-butyl ester have so far not been carried out free of a heterogeneous component.[10]

TABLE 4

Rate ratios at 600 K for pyrolysis of various compounds [1,7-10]

Compound	Pr^i/Et	Bu^t/Pr^i	$10^3k/s^{-1}$ for Bu^t compound at 600 K [a]
Vinyl ethers	10	17.8	7.68
Thiolacetates	17	76.5	1.42
2-Alkoxypyridines	18	91.4	20.1
Acetates	28.8	115	32.5
Phenylacetates	32.3	121	55.6
Benzoates	36.3	125	76.3
Phenyl carbonates	39.8	126	583
Trifluoroacetates	47.2	135 [b]	817 [b]
Bromides	261	250	0.042

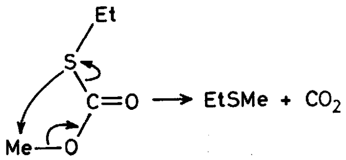
[a] Some of these values differ slightly from those given in ref. 7 as a result of thermocouple recalibration (see ref. 1). [b] Calculated value, see text.



Correlation of rate ratios for pyrolysis of various compounds

Another factor (to which we have previously drawn attention) [10] is now more evident from the extended data in Table 4. For all the compounds for which C–O bond breaking is the most important rate-determining step, the extent of transition state polarity (measured by the rate ratios) is paralleled by the reactivity of the compound class (measured in terms of the elimination rate coefficient for the t-butyl compound). This in itself confirms that all the compounds have a similar rate-determining step, and seems sufficiently well established now for the correlation to be used for predictive purposes. A similar correlation may in time be found for compounds for which C–S and C–N bond breaking are the principal rate-determining steps.

One set of data are completely at variance with the above analysis of Pr^i/Et and Bu^t/Pr^i rate ratios, namely those obtained from pyrolysis of *S*-alkyl *O*-methyl carbonates.[13] These give an overall rate spread (Bu^t/Et) of 2 540 at 600 K, smaller than for phenyl carbonates as expected (*cf.* thiolacetates *versus* acetates). However the Pr^i/Et ratio is anomalously large (75) and much larger than the surprisingly small Bu^t/Pr^i ratio (34). This suggests that some of the Arrhenius data may be in error (no rate coefficients were reported), especially since the difference between the activation energies for the *S*-alkyl *O*-methyl carbonates and phenyl carbonates [7] or methyl carbonates [14] (which themselves agree to ± 0.3 kcal mol^{-1} for like compounds) is much higher for the ethyl compound (9 kcal mol^{-1}) than for the isopropyl and t-butyl compounds (5.5 kcal mol^{-1} for each). Moreover the log *A* value for the ethyl compound was higher than for the isopropyl and t-butyl compounds whereas it is usual for the ethyl value to be lower. From the data for other ethyl compounds we would expect *E* 50.5 kcal mol^{-1} and log *A* 11.7 s^{-1} for *S*-alkyl *O*-methy carbonate. The anomaly cannot be due to incursion of a different elimination mechanism because this would have to be energetically more favourable and therefore necessarily show up as an increased rate, particularly for the *least reactive* compound, exactly the opposite of that which is observed. The results can however follow from a previous observation of one of us that carbonates can undergo nucleophilic substitution in the gas phase (S_Ni reaction).[15] This has a higher activation energy than elimination and is unimportant for carbonates at *ca.* 600 K. However for thiolcarbonates the greater nucleophilicity of sulphur may enhance the substitution (III) to the extent that it competes with the elimination, especially at the very high temperatures (820 K) used in the kinetic study. Indeed there has been a report of just such a reaction (in polar aprotic solvents at 170 °C) for thiolcarbonates.[16] If an elimination (stoicheiometry 3.0) is accompanied by a slower substitution (stoicheiometry 2.0), the derived kinetic plot will appear to be first-order for at least three half-lives giving an intermediate rate coefficient, and the lower stoicheiometry might escape detection. Such a reaction will be much less significant for the secondary and tertiary thiolcarbonates because the elimination rates will be so much faster, whereas the substitution is likely to be of comparable rate. Thus it would seem appropriate to use these results with caution at present.



(III)

The Effect of β-*Substituents*.—Previous data indicated that n-butyl vinyl ether pyrolysed more rapidly than ethyl vinyl ether [2,3,17] and our data (obtained under identical conditions for both compounds, Table 2) confirms this. These show that a β-ethyl substituent accelerates the elimination 1.52-fold at 600 K ≡ 2.28-fold per β-hydrogen; this compares with 1.62-fold per β-hydrogen for acetates at the same temperature.[18] The latter we have attributed to steric acceleration [18] which may also account for the vinyl ether results. However, it is not possible to discount the recently identified electron acceptance by alkyl groups when attached to saturated sites (in the gas phase), in contrast to their electron-supplying effect when attached to unsaturated sites.[19] Since the effect of methyl attached to the β-carbon is opposite to that when in the *para*-position of a β-phenyl substituent this explanation would also account for the acetate results.[18]

A β-chloro substituent decreases the rate of ethyl vinyl ether pyrolysis [5] by a factor of 0.54 per β-hydrogen at 600 K, precisely the same as in acetate pyrolysis.[1,18,20] A β-substituent of the $-I$, $+M$ type acts in three ways.[18] (a) The $-I$ effect increases the acidity of the β-hydrogen and hence the rate. (b) The $+M$ effect decreases the acidity of the β-hydrogen and hence the rate. (c) The $-I$ effect weakly destabilizes the remote incipient α-carbocation and decreases the rate. For a strong $-I$ group such as chlorine, effect (c) evidently dominates for both eliminations.

Direction of Elimination.—DePuy and King [21] showed that 1-methylpropyl vinyl ether gives a different product distribution from 1-methylpropyl acetate [22] (Table 5), and we can now rationalise this. Previously one of us demonstrated that as an *Ei* transition state becomes more *E*1-like, *i.e.* as the importance of β-C–H bond breaking diminishes in the corresponding reactions, two features emerge. (a) The proportion of terminal alkene diminishes and (b) the proportion of the *trans*-internal alkene increases.[23] Now the spread of rates in Table 4 shows that the transition state for vinyl ether pyrolysis is neither more polar nor therefore more *E*1-like than that for acetate pyrolysis. However, because the $C=CH_2$ group is less nucleophilic than the C=O group, β-C–H bond breaking must be less kinetically significant so that the product distribution should nevertheless be more '*E*1-like.' This is precisely observed.

TABLE 5

Elimination from 1-methylpropyl compounds (%)

	But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene
Acetate	57	28	15
Vinyl ether	47	37	16

The Relative Rates of Ester and Vinyl Ether Pyrolyses.—Bailey and Di Pietro claimed that vinyl ethers pyrolyse 50° below the corresponding esters.[24] This statement could only apply if the activation energies for both types of compounds were the same (which they are not), and if the spread of rates (arising from the transition state polarity) was the same in both reactions; the data in Table 4 show this also to be untrue. The relative rates of vinyl ether to acetate pyrolysis at 600 K are: 4.40 (Et); 1.53 (Pr^i); 0.24 (Bu^t). Thus only the primary vinyl ether is significantly more reactive than the ester (corresponding to a 25° difference in temperature to produce a comparable rate), whilst the tertiary vinyl ether is considerably *less* reactive than the ester, and indeed requires a 25° *greater* temperature to achieve the same elimination rate.

EXPERIMENTAL

Ethyl vinyl ether was obtained by fractionally distilling a commercial sample, in order to remove the stabilizer. Isopropyl vinyl ether and t-butyl vinyl ether was obtained by the transetherification method,[5,25] except that n-butyl vinyl ether was used as the exchanging ether since it is commercially available. This has a slight disadvantage in making isolation of the t-butyl vinyl ether more difficult since the b.p. of 77 °C is close to that of the byproduct n-butanol (82 °C). However by resubjecting the lowest boiling fraction to re-etherification (twice) the pure compound, n_D^{20} 1.3970, could be obtained. n-Butyl vinyl ether was obtained by fractionally distilling a commercial sample.

Kinetic Studies.—The general method of pyrolysis has been described.[26]

[1/1566 *Received*, 8*th October*, 1981]

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