686. *Gas-phase Eliminations. Part I. The Unimolecular Gas-phase Pyrolysis of Some Esters and Analogous Compounds.**

By Allan Maccoll.

Points of similarity and dissimilarity between the effects of α-methylation upon the rates of unimolecular pyrolysis of alkyl halides and of alkyl esters in the gas phase are discussed. It is suggested that gas-phase eliminations may be classified according to the importance of the bonds which are (*a*) broken or (*b*) formed in the transition state. When the two types are of roughly equal importance the reaction may be regarded as essentially homolytic. When the breaking bond, as in the case of the alkyl halides, or the forming bond as in the case of the esters, controls the reaction, and if the transition state is essentially polar, the mechanism is best thought of as being analogous to that of certain heterolytic reactions in solution.

The resemblance, shown in the literature, between the pyrolysis of esters and reactions of the corresponding halides is not surprising, since the reactions are formally similar: $>\mathrm{CH{-}CX}< \longrightarrow >\mathrm{C{=}C}< + \mathrm{HX}$, where X is acyloxy or halogen. The analogy recently postulated[1] between homogeneous unimolecular dehydrohalogenation in the gas phase and substitution and elimination in a polar solvent raises the question how far similar mechanistic concepts apply to ester pyrolysis.

For pyrolysis of alkyl bromides two broad conclusions have emerged: (*a*) that elimination from primary alkyl bromides occurs by a mixed chain and unimolecular mechanism,[2, 3] the former being effectively inhibited by *cyclo*hexene,[3, 4] whereas (*b*) that from secondary[5] and tertiary bromides[6] is predominantly by a unimolecular mechanism.

Makens and Eversole[7] have studied ethyl formate, and Anderson and Rowley[8] *n*- and *iso*-propyl formate. Blades[9] has used the toluene-inhibition flow-technique to investigate ethyl formate and *iso*propyl formate. The Arrhenius parameters are as tabulated:

	Ethyl formate		*iso*Propyl formate	
E (kcal./mole)	40·01	44·14	44·23	44·0
$10^{-13} A$ (sec.$^{-1}$)	$2{\cdot}52 \times 10^{-4}$	0·0213	0·247	0·38

For *n*-propyl formate, E (39·7 kcal. mole^{-1}) and A ($2{\cdot}94 \times 10^{9}$ sec.$^{-1}$) are very close to those for ethyl formate. It appears then, that primary esters undergo elimination by a mixed chain and unimolecular mechanism, as is the case for bromides.

Arrhenius parameters for the unimolecular decompositions of esters $\mathrm{R{\cdot}CO_2R'}$ are set out in Table 1. From these, relative rates at 400° have been calculated, *viz.*: for variation of R, $\mathrm{EtOAc/H{\cdot}CO_2Et}$ 0·97, $\mathrm{Pr^iOAc/H{\cdot}CO_2Pr^i}$ 1·25, $\mathrm{Et{\cdot}CO_2Bu^t/Bu^tOAc}$ 0·79; for variation of R′, $\mathrm{Pr^iOAc/EtOAc}$ 26, $\mathrm{Bu^tOAc/EtOAc}$ 515; $\mathrm{H{\cdot}CO_2Pr^i/H{\cdot}CO_2Et}$ 20, $\mathrm{H{\cdot}CO_2Bu^t/H{\cdot}CO_2Et}$ 720. Two conclusions can then be drawn: (*a*) variation of the group R has only a small effect on the rate, *i.e.*, the rate at which an ester decomposes is nearly independent of the acid from which it is derived (cf. Warwick and Fugassi[12]); (*b*) variation of group R′ has a marked effect, the esters being divided into three classes

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* The subject matter of this paper was presented at the XVIth Internat. Congr. Pure Appl. Chem., Paris, 1957.

[1] Maccoll and Thomas, *Nature*, 1955, **176**, 392.
[2] Agius and Maccoll, *J.*, 1955, 973; Semenov, Sergeev, and Kapralova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 301.
[3] Maccoll and Thomas, *J.*, 1957, 5073.
[4] (*a*) Thomas, (*b*) Harden and Maccoll, (*c*) Green, Maccoll, and Thomas, unpublished work.
[5] Maccoll and Thomas, *J.*, 1955, 979, 2445.
[6] Harden and Maccoll, *J.*, 1955, 2454; 1957, 5028; Harden, *J.*, 1957, 5024.
[7] Makens and Eversole, *J. Amer. Chem. Soc.*, 1939, **61**, 3203.
[8] Addison and Rowley, *J. Phys. Chem.*, 1943, **47**, 454.
[9] Blades, *Canad. J. Chem.*, 1954, **32**, 366.

depending upon whether the α-alkyl-carbon atom is primary, secondary, or tertiary, the rates for these differing by somewhat more than an order of magnitude.

TABLE 1. *Arrhenius parameters for unimolecular decomposition of esters* $\text{R}\cdot\text{CO}_2\text{R}'$.

R	R′	log *A*	*E* (kcal./mole)	Ref.	R	R′	log *A*	*E* (kcal./mole)	Ref.
H	Et	11·33	44·1	9	Me	Pr^{i}	13·00	45·0	9
H	Pr^{i}	12·58	44·0	9	Me	Bu^{t}	12·80	39·2	11
		12·33	44·2	8	Et	Bu^{t}	13·34	40·5	12
H	Bu^{t}	11·10	34·6	10	Ph	Menthyl	11·00	38·1	13
Me	Et	12·49	47·8	9					

TABLE 2. *Relative rates of pyrolysis at* 400°.

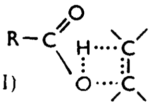
Class	Et	Pr^{i}	Bu^{t}	Ref.	Class	Et	Pr^{i}	But	Ref.
Chlorides ...	1	178	19,500	1	Acetates	1	26	515	9, 11
Bromides ...	1	170	32,000	1	Formates	1	20	720	8, 9, 10

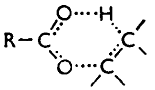
The relative rates for the esters are compared in Table 2 with those for the chlorides and bromides. The trends are similar, suggesting an underlying common effect of α-methyl substitution. However the effect is much smaller for esters and, as will be seen below, this provides a clue to the mechanism. It is interesting that in each case the rate ratio for the *tert.*-butyl compound is approximately the square of that for the *iso*propyl compound, indicating that the effect is approximately linear with respect to the activation energy.

Szwarc and Murawski[14] have shown that acetic anhydride decomposes cleanly and by a unimolecular mechanism to acetic acid and keten. The rate constant is given by $\log k_1 = 12{\cdot}1 - 34{,}500/2{\cdot}303\boldsymbol{R}T$. The activation energy is about 13 kcal. less than for ethyl acetate. The rate ratio with respect to ethyl acetate is 5600.

In a series of papers on the pyrolysis of esters in a flow system, Bailey and his colleagues[15] report that the olefin produced is the ethylene that carries the least number of alkyl substituents. Thus, *sec.*-butyl acetate would yield predominantly but-1-ene, while *tert.*-amyl acetate would yield 2-methylbut-1-ene. Bailey has pointed out that gas-phase elimination from esters follows the Hofmann rule.

The salient features that emerge from a survey of known unimolecular eliminations from esters are: (1) The rate sequence is $\text{Me}_3\text{C} > \text{Me}_2\text{CH} > \text{Me}\cdot\text{CH}_2$, but with a very much reduced spread than for halides. (2) The direction of elimination is governed by the Hofmann rule, in distinction to the behaviour of alkyl halides in the gas phase. (3) Acetic anhydride decomposes much faster than ethyl acetate. Before considering these facts in the light of electronic theory, previous ideas on the nature of the transition state in ester eliminations require mention. Two transition states have been suggested, namely, (I) and (II), involving respectively four and six centres. Warwick and Fugassi[21] dismiss (I) on the grounds that the pre-exponential term in the Arrhenius equation should be low, that is considerably less than the "normal" value of 10^{13} sec.$^{-1}$. Superficially this argument appears to be invalidated by the behaviour of the halides, for which the frequency factors are $\sim 10^{13}$ sec.$^{-1}$. However, in this case, the transition state is best regarded as a pseudo-four-centre system, to which the idea of rigidity and consequent large negative entropy of activation does not apply. On the other hand, formulation (II) is


(I)


(II)

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[10] Gordon, Price, and Trotman-Dickenson, *J.*, 1957, 2813.

[11] Rudy and Fugassi, *J. Phys. Chem.*, 1948, **52**, 357.

[12] Warwick and Fugassi, *ibid.*, 1948, **52**, 1314.

[13] Barton, Head, and Williams, *J.*, 1953, 1715.

[14] Szwarc and Murawski, *Trans. Faraday Soc.*, 1951, **47**, 268.

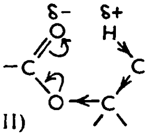
[15] Bailey and King, *J. Org. Chem.*, 1956, **21**, 858, and references cited there.

favoured by the largely unstrained six-membered ring, and subsequent discussion will be built on the basis of (II).

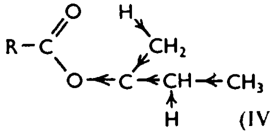
The key to the electronic interpretation of the reaction is Bailey's observation that the olefin production is governed by the Hofmann rule. In discussing elimination from sulphonium salts by the bimolecular mechanism (*E*2), Ingold[16] pointed out that the observed Hofmann orientation implies inductive control of the reaction. Three pieces of evidence suggest that this also applies to ester pyrolysis in the gas phase: (*a*) the Hofmann orientation; (*b*) a surprising analogy in the effect of α-methyl substitution in the two cases (cf. Table 3); (*c*) the marked effect of the carbonyl group in acetic anhydride (see above) (Me·CO·O·**CO**·Me *versus* Me·CO·O·**CH$_2$**·Me), replacement of CH$_2$ by CO causing a strong inductive withdrawal of electrons from the β-hydrogen atom which, as will be seen below, will augment the effect of the carbonyl-oxygen atom. This evidence suggests that the reactions are best considered as a nucleophilic attack of the acyl-oxygen atom on the β-hydrogen atom. In other words, it is the *forming* O–H bond that primarily determines the rate, and not the breaking alkyl–oxygen bond. The transition state may then be represented as (III). α-Methyl substitution would tend to stabilise such a transition state, accounting for the increase in rate in the α-methylated series. The effect of β-methylation in producing the greater proportion of the terminally unsaturated olefin is explained by the inductive protective action of the β-methyl group on the *sec.*-C–H bond[16] [(cf. (IV)]. It will be noted that the mechanism suggested for the esters is in marked contrast with that postulated for halides, where the dominating factor is the *breaking* C–X bond.

TABLE 3. *Relative rates in gas-phase and E2 eliminations.*

Compound	Ethyl	*iso*Propyl	*tert.*-Butyl
Formate (400°)	1	20	720
Acetate (400°)	1	26	515
Alkylsulphonium ion (45°)	1	23	586

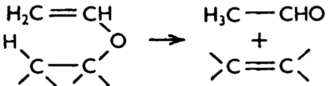


(III)



(IV)

A further reaction for which a six-centred transition state has been postulated, and which shows a quantitative analogy with the pyrolysis of esters, is pyrolysis of alkyl vinyl ethers. *n*-Butyl and *iso*butyl vinyl ether have been shown by Molera and Quiros[17] to decompose by a mixed chain and unimolecular mechanism (cf. primary bromides and esters). In two cases the unimolecular elimination reactions have been isolated, namely



(V)

for ethyl vinyl[18] (V) and *iso*propyl vinyl ether.[19] The reaction is clean, and follows the annexed scheme. The Arrhenius parameters are compared in Table 4 with those of the corresponding esters. The rate ratios of the *iso*propyl to the ethyl compound are respectively 20 and 17. This evidence suggests a similarity of mechanism. Since ethyl formate and ethyl vinyl ether differ only by the replacement of an oxygen atom by a

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[16] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

[17] Molera and Quiros, XVIth Internat. Congr. Pure Appl. Chem., Paris, 1957.

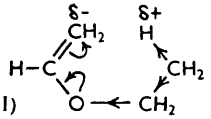
[18] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1039; cf. Wang and Winkler, *Canad. J. Res.*, 1943, **21B**, 97.

[19] Blades, *Canad. J. Chem.*, 1953, **31**, 418.

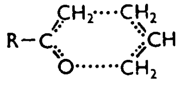
methylene group [H·CO·OEt, H·C(:CH_2)·OEt]. The conclusion is that the reaction is essentially a nucleophilic attack on the β-hydrogen atom by the $CH_2^{\delta-}$ group as shown in the representation (VI). The behaviour of alkyl vinyl ethers contrasts sharply with that of diethyl ether or divinyl ether,[20] for which no such mechanism is possible. Diethyl ether[21] decomposes in part by a chain mechanism, whereas pyrolysis of divinyl ether is by a complex mechanism, involving free radicals.[22]

TABLE 4. *Arrhenius parameters for pyrolysis of formates and vinyl ethers.*

	Formate		Vinyl ether	
	log *A*	*E* (kcal./mole)	log *A*	*E* (kcal./mole)
Ethyl	11·33	44·1	11·43	43·6
*iso*Propyl	12·58	44·0	12·58	43·6



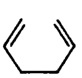
(VI)

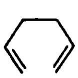


(VII)

The reactions of allyl vinyl[23] and allyl *iso*propenyl ether[24] have also been studied in the gas phase. These compounds rearrange at roughly the same rate, to give pent-4-enal and hex-5-en-2-one, respectively, the suggested transition state being (VII). This similarity in rate might be expected since the only difference is methyl-substitution at the centre of a three-atom mesomeric system. The Arrhenius parameters reported were 30·6 kcal./mole and 5×10^{11} sec.$^{-1}$, and 29·3 kcal./mole and $5{\cdot}4 \times 10^{11}$ sec.$^{-1}$, respectively. It is of interest that allyl *p*-tolyl ether rearranges in solution in diphenyl ether with Arrhenius parameters of roughly the same value (33·1 kcal./mole and $1{\cdot}6 \times 10^{11}$ sec.$^{-1}$).[25] No data exist to show the effect of α-methylation in the allyl group.* It can be suggested that in reactions of this type both the forming and the breaking bond are of importance in determining the kinetics of the reaction, as has indeed been done by Ingold.[16]

This raises the question of the possibility of distinguishing between homolytic and heterolytic mechanisms in cyclic transition states. Hughes and Ingold,[26] referring to reactions proceeding in solution through a cyclic transition state, state that " it is unphysical to try to classify intramolecular rearrangements as exclusively electrophilic or nucleophilic or even heterolytic or homolytic . . . though cases may arise in which one character seems to predominate." The present discussion points out some cases in which the distinction can reasonably be made for gas-phase reactions. In general, if the cyclic transition state of a gas reaction can be represented by the structures (VIII) and (IX),

(VIII)



(IX)

then the reaction may be best thought of as essentially homolytic. This is the case in which the forming and the breaking bond are of roughly equal importance. However,

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* *Added, July 21st*, 1958.—Goering and Jacobson (*J. Amer. Chem. Soc.*, 1958, **80**, 3277) have shown that α-methyl substitution increases the rate of rearrangement of allyl phenyl ethers in solution fourteenfold, as predicted by Rhoades and Crecilius (*ibid.*, 1955, **77**, 5057). I thank Professor H. L. Goering for sight of the manuscript before publication.

[20] Taylor, *J. Chem. Phys.*, 1936, **4**, 116.

[21] Smith and Hinshelwood, *Proc. Roy. Soc.*, 1942, *A*, **180**, 237; Steacie, " Atom and Free Radical Reactions," Reinhold, Publ. Inc., New York, 1954.

[22] Lossing, Ingold, and Henderson, unpublished work, referred to by Steacie.[21]

[23] Schuler and Murphy, *J. Amer. Chem. Soc.*, 1950, **72**, 3155.

[24] Stein and Murphy, *ibid.*, 1952, **74**, 1041.

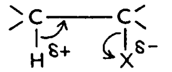
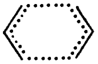
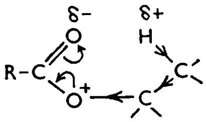
[25] Kinkard and Tarbell, *ibid.*, 1939, **61**, 3085.

[26] Hughes and Ingold, *Quart. Rev.*, 1952, **6**, 34.

if the transition state is essentially characterized by a breaking bond (alkyl halides) or a forming bond (esters) and if this process is essentially polar in character, then it is reasonable to regard them as essentially heterolytic and to discuss the effect of structural variations in terms of the well-developed theories of organic reactions in solution.

This discussion may be summarized as in Table 5.

TABLE 5. *Transition states in gas-phase reactions.*

Type of reaction	Transition state	Solution analogue
Olefin elimination from halides		S_N1
Claisen rearrangement		Similar to gas-phase, in non-polar solvents
Olefin elimination from esters		*E*2

Claisen-type rearrangement seems to involve a roughly equal status for the forming and the breaking bond. In the two extreme cases, halides and esters, α-methyl substitution alters the rate by one or two orders of magnitude respectively. A question, as yet unanswered, then arises whether the effect of such substitution in the intermediate case will lie between the two extreme ones or will be unrelated to either.

Conclusion.—This discussion bears out Maccoll and Thomas's general conclusion[1] that certain homolytic gas-phase reactions can be usefully discussed in terms of mechanism and structural effects that have been firmly established for heterolytic reactions in polar solvents, and that these reactions can be classified by the relative importance of bond-breaking and bond-forming in the transition state.

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