Thermolysis of Allylic Formates

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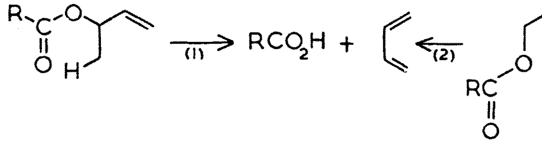
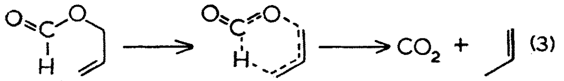
Summary Carbon dioxide and olefins are the products of a new thermal reaction of allylic formates.

ALLYLIC esters rearrange on heating,[1] usually above 300° and in the gas phase, most if not all of the rearrangement of the allyl group occurring *via* its intramolecular migration to the acyl oxygen atom.[2] A competing decomposition (1) to diene and carboxylic acid occurs[1,2] if hydrogen of an alkyl substituent at the α-position is available for abstraction by the acyl group *via* the usual six-centred transition state for ester elimination.[3] For αβ-dimethylallyl acetate, Lewis and his co-workers[2] have shown that rearrangement and the elimination (1) occur at comparable rates. For a *cis*-γ-alkyl substituent a third cyclic mechanism (2) may be possible, as has been suggested for elimination from γ-methylallyl chloride.[4]

We report that a fourth reaction can occur for allylic formates. The formation of nearly equimolar amounts of propene and carbon dioxide from allyl formate in the gas phase above 365° is an example of this new reaction (3), for which we envisage an intramolecular mechanism involving 1,5-transfer of the formyl hydrogen atom as shown. A similar elimination reaction of allylic chloroformates accounts for the formation of carbon dioxide and rearranged allylic chloride.[5] There is a further analogy to the thermal decompositions of alkyl vinyl ethers[6] and of β-hydroxy-olefins.[7]

Manometric studies of allyl formate pyrolysis in a static system between 405—465° reveal good first-order kinetics up to at least two-thirds reaction. G.l.c. analysis of the volatile products shows propene, carbon dioxide (the partial pressure of which closely follows the increase in total pressure), and smaller amounts of methane, hydrogen, and carbon monoxide. The decomposition rate shows little sensitivity to variation in the surface/volume ratio of the reaction vessel, and is unaffected by the addition of nitrogen (up to 200 mm. with 30 mm. allyl formate at 445°).





From the temperature dependence of the initial rate of pressure increase, we find an activation energy of 43·15 ± 0·66 kcal. mole^{-1} and a frequency factor (A) of $10^{10\cdot0\pm0\cdot2}$ sec.$^{-1}$, which corresponds to an activation entropy of −14·6 ± 1·1 e.u.

trans-Cinnamyl formate is similarly decomposed at

332—342° to carbon dioxide and allylbenzene. β-Phenylallyl formate is also decomposed in the temperature range 350—410°, but less cleanly: alongside the expected α-methylstyrene appears acetophenone, the origin of which is not yet clear.

Processes involving 1,5-transfer of hydrogen to an olefinic carbon atom also occur in the mass-spectral fragmentation (McLafferty rearrangement) of the molecular ions of allyl and benzyl ethers, β-hydroxy-olefins, alkenes, and alkylbenzenes.[8] However, transfer of a formyl hydrogen atom, as in (3), is apparently unimportant: in the mass spectrum of allyl formate there is an insignificant peak for $C_3H_6^+$ (*m/e* 42), but instead the base peak (*m/e* 57) corresponds to the loss of CO + H from the molecular ion as characteristic of formate esters.

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