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GAS PHASE THERMOLYSIS OF ALLYLIC FORMATES

KINETICS AND ISOTYPE EFFECTS*

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Abstract—Allyl and methallyl formate are observed to thermally cleave in the gas phase to carbon dioxide and olefin with $E_A = 43{\cdot}0$ and $42{\cdot}1$ kcal mole^{-1} and log $A = 10{\cdot}1$ and $9{\cdot}8$ respectively. This kinetic data and evidence from isotopic labeling with tritium and deuterium reveals that the rearrangement does not involve a radical chain. The rate of the much faster Cope-type allylic ester rearrangement of allyl-1,1-d$_2$-formate to allyl-3,3-d$_2$-formate was also determined.

PRECEDING PAPERS IN THIS SERIES[1] have studied the rates of gas phase intramolecular isomerizations of allylic esters, reaction 1. These rearrangements are homogeneous, intramolecular and reversible. Substituent effects support a transition state possessing substantial charge separation with positive charge on the allylic portion and negative charge on the carboxylate moiety.

R = H, D, Me, CF_3
X = Cl, CF_3, Me, Me (1)

Allylic chloroformate esters isomerize *via* a Cope-type mechanism analogous to the other substituted carboxylates, and in addition decompose by S_Ni and S_Ni' processes to the chloride and CO_2.[2] Further study of these mechanisms proved to be unpromising due to competing elimination reactions and heterogeneous contributions.

We have discovered similar S_Ni or S_Ni' decomposition mechanisms for the gas phase pyrolysis of allylic formate esters and have made a kinetic study of two cases, allyl and methallyl formate. The S_Ni' fragmentation yielding olefin and CO_2 is formally a retroene reaction, an intramolecular, heteronuclear variant of the symmetry allowed 1,5-hydrogen shift.[3] In addition, the rate of the formate allylic ester isomerization *via* the "1,3-dioxa-Cope" mechanism was determined for allyl-1,1-d$_2$-formate. Allyl and methallyl formate were chosen for study because of their ready availability, ease of isotopic labeling, and freedom from complicating side reactions. During the course of this work another study of the gas phase pyrolysis of allyl formate in a static reactor was reported.[4]

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* This is Part V in the series *The Rearrangement of Esters in the Gas Phase*; Part IV, E. S. Lewis and J. T. Hill *J. Am. Chem. Soc.* **91**, 7458 (1969).

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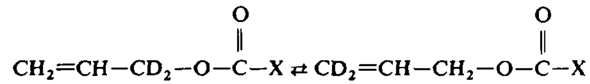
RESULTS

The rearrangement of allyl-1,1-d_2-formate was followed in the stirred flow reactor previously described.[1, 2] except that the reaction vessel was made of quartz. The reactor was well seasoned with unlabeled material prior to addition of the deuterium labeled compound. After sufficient time had elapsed to ensure that a steady state was obtained, the ester in the effluent gas stream was trapped at −78°C and analyzed by NMR. The first order rate constants for rearrangement are $k = 2{\cdot}9 \times 10^{-5}\ \text{sec}^{-1}$ at 324·9°C* and $k = 2{\cdot}3 \pm 0{\cdot}8 \times 10^{-4}$ at 368·8°C.† Sufficient data were not collected to define the Arrhenius constants well, but the rate constants are quite reasonable compared with other systems (Table I).

Table I summarizes the effect of carboxyl substituents on allylic ester rearrangements and shows that all data are consistent with the previously proposed polar transition state.

Table I. Relative rates for the gas phase rearrangement of allylic esters at 325°C.[1]



$$CH_2{=}CH{-}CD_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X \rightleftarrows CD_2{=}CH{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X$$

Substituent (X)	k/k (allyl formate)[c]	Taft σ_I
CF_3[a]	128·0	0·41
MeO[b]	6·5	0·25
H[a]	1·0	0·0
Me[b]	0·4	−0·05

[a] A deuterium label was used.

[b] These rates were estimated from data on crotylesters assuming that the Me group accelerates these reactions by the same amount that it does in allyltrifluoracetate.

[c] This work.

The rates obtained for the first-order fragmentation of allyl formate to propene and CO_2 and of methallyl formate to isobutene and CO_2 are given in Table II.

Rates were determined using the stirred flow reactor and gas chromatographic analysis of the effluent vapors. In addition to propene and isobutene small amounts (never greater than 7% of the major olefin peak area) of other hydrocarbon gases including methane and allene were found. In addition, in an unseasoned reaction flask significant amounts of methallyl alcohol were produced by a heterogeneous process. This product could be completely eliminated by seasoning.

Allyl formate-d_1 and unlabeled allyl formate were pyrolyzed together at 444°C to 54% reaction. Formyl deuterium content in the starting mixture was 32·9 ± 0·4% and 33·5 ± 0·3% in the exit vapors by NMR. Thus, within experimental error there is a negligible deuterium isotope effect.

Tritium labeled methallyl formate-t_1 was pyrolyzed and the unreacted ester

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* Average of two runs.

† Average of three runs; experimental error was large here because of the small amount of starting material available.

TABLE II. RATES OF ALLYLIC FORMATE DECOMPOSITION

Compound	Temp. °C	$k \times 10^4$ sec^{-1} (av)[a]	Log A	E_A, kcal/mole^{-1}
Allyl Formate	401·5	0·96	10·1 ± 0·3	−43·0 ± 0·9[b]
	414·0	2·30		
	426·0	3·83		
	437·5	6·65		
	449·1	12·0		
	465·0	20·0		
	492·2	54·7		
Methallyl Formate	398·2	1·57	9·8 ± 0·6	−42·1 ± 1·0
	414·5	2·80		
	423·2	4·05		
	441·2	9·97		
	454·0	15·5		
	460·2	23·0		

[a] The rate constants presented are the average of from 3–7 values collected at different flow rates. The standard deviation from the mean of these rate constants is usually less than 6 per cent.

[b] This compares very favorably with Vernon's value[4] of $E_a = -43{\cdot}15 \pm 0{\cdot}66$ kcal/mole and log $A = 10{\cdot}0 \pm 0{\cdot}2$.

recovered. The tritium content of the unreacted material determined by a Tri-carb Liquid Scintillation Spectrometer yielded a tritium isotope effect of 1·04 = 0.02.

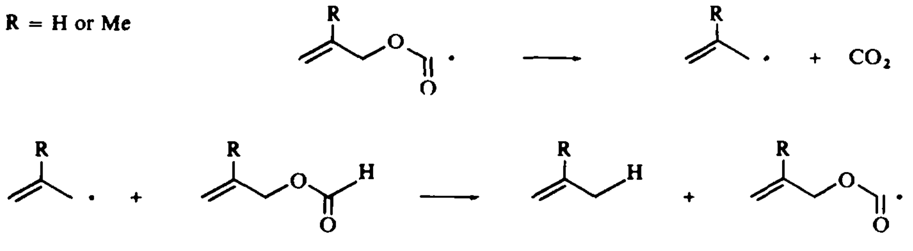
Pyrolysis of a mixture of allyl and methallyl formate demonstrated that methallyl formate is 2·1 times more reactive. When a mixture of methallyl formate-t_1 and allyl formate were pyrolyzed together and the effluent propene and isobutene trapped as the dibromides by bubbling through a bromine in heptane trap at −10°C, the 1,2-dibromopropane isolated by preparative VPC was virtually non-radioactive. All tritium activity could be accounted for as arising from minor products of the methallyl formate-t_1 decomposition.

DISCUSSION

Whereas the "1,3-dioxa-Cope" isomerization *via* an intramolecular, homogeneous, polar transition state appears well established, the mechanism for the retro-ene decomposition of the above formate esters is not so well grounded.[3] Previous workers[4] have reported that in a static reactor allyl formate decomposes by a first order process that is insensitive to surface to volume changes in a well-seasoned reactor. There was no evidence however to rule out a likely radical chain process (Scheme I).

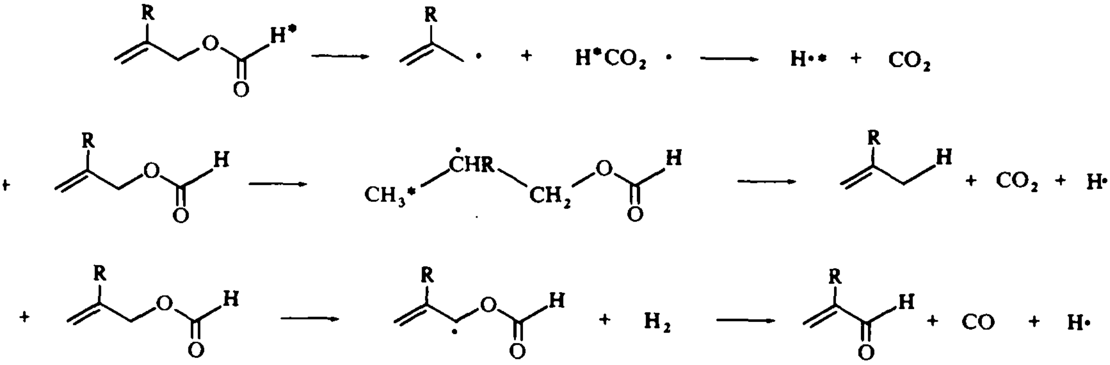
SCHEME 1

R = H or Me



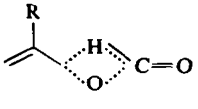
Evidence from the experiment to look for crossed products in the decomposition of a mixture of methallyl formate-t_1 and allyl formate indicates that no more than a small fraction of the reaction follows the route in which an allyl or methallyl radical abstracts a hydrogen atom from the formyl position of another molecule of ester. The propene trapped contained less than one per cent of the tritium label present in the methallyl formate-t_1. This result likewise argues against another likely radical mechanism involving allyl-oxygen cleavage followed by induced radical decomposition *via* addition to the double bond or abstraction of a Δ-hydrogen from the allyl position (Scheme II). (Louw and Kooyman have reported that this is a common radical reaction for allyl esters at 485°C and is virtually independent of the acyl moiety.)[5] However, this process could be a side reaction, for Vernon reported[4] that small amounts of CO and H_2 were formed in their reactions. These products would not be observed by our analytical technique using a hydrogen flame ionization detector.

SCHEME 2



The concerted, intramolecular retro-ene process remains an attractive possibility for the reaction mechanism. It is consistent with the observed first-order kinetics and the absence of cross-products. The activation parameters (determined by two different techniques for allyl formate)[4] are similar to those found for other retro-ene reactions studied. Ethyl vinyl ether cleaves to acetaldehyde and ethylene with $E_{\text{A}} = -43{\cdot}8$ kcal mole^{-1} and log $A = 11{\cdot}4$[6] and 1-phenyl-4-ethyl-4-hydroxyhex-1-ene fragments to diethylketone and 3-phenylpropene with $E_{\text{A}} = -41{\cdot}8$ kcal mole^{-1} and log $A = 12{\cdot}0$[7]. Furthermore, although the isotope effects found are small or virtually non-existent, this is not unreasonable if the transition state is non-linear or very unsymmetrical. Indeed, this appears to be the case for another retro-ene reaction: allyl α-deuterodiphenylmethyl ether gave an isotope effect of only 1·1 ± 0·1 at 430°C.[8]

Another type of intramolecular mechanism conceivable is the S_{Ni} 4-centered process. While this mechanism cannot definitely be discounted, since the interconversion of allylic isomers is too fast, the pre-exponential factor found for both of the



formate esters is in much closer agreement with those generally found in 6-centered transition states.[9] Furthermore, orbital symmetry arguments require a difficult transition state geometry.

EXPERIMENTAL

Allyl and methallyl formate. Conventional Fischer esterification of commercial materials was used. Purification was by spinning bond distillation or preparative VPC on a Carbowax 20M column.

Allyl-α-d_2 formate. Allyl-α-d_2 alcohol was prepared by the reduction of acryloyl chloride with LAD.[10] Fischer esterification with formic acid gave the ester which was then purified by preparative VPC. The methylene doublet at $\delta = 4{\cdot}7$ (from TMS) shown by the undeuterated sample was almost absent in this sample; integration of this almost absent peak compared to the complex three proton multiplet between $\delta = 5{\cdot}1$ and $6{\cdot}3$ showed that it was 98·6% deuterated.

Allyl formate-d_1. Formic acid-d_2 was prepared from oxalic acid which had been exchanged several times with D_2O. Upon pyrolysis at 180–210°C at reduced pressure, the evolved formic acid-d_2 vapor was condensed and trapped. The ester was then prepared by Fischer esterification with allyl alcohol.

Methallyl formate-t_1. Formic acid-t_2 was prepared as above from oxalic acid which had been exchanged with tritiated water. (New England Nuclear.) This was then esterified with methallyl alcohol.

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