Evidence for a Novel α-Elimination Mechanism in Gas-phase Thermolysis of Esters

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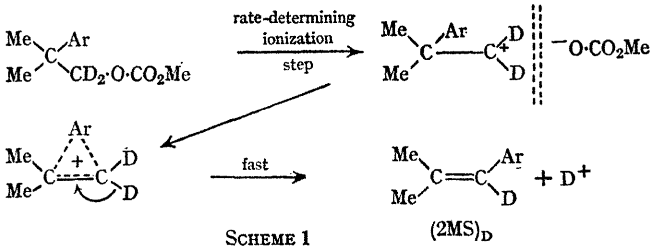
Gas-phase thermolyses of neophyl (2-methyl-2-phenylpropyl) esters (including acetate and carbonate) takes place with Wagner–Meerwein rearrangement to give an excess of of the unconjugated olefin 2-benzylpropene (BP).[1] The olefin components of this rearrangement are the result of nearly exclusive phenyl migration. These results are quite unlike those obtained in the liquid phase reaction,[2] where the conjugated product, ββ-dimethylstyrene (2MS), is formed in *ca.* ten times the amount of the unconjugated.[1]

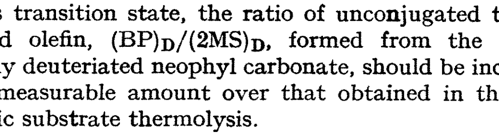
This degree of formation of the unconjugated isomer was previously[1] interpreted as evidence of an unusual 7-membered cyclic, concerted transition state, though how the remainder (44% at 575°) of rearrangement product, (the conjugated olefin 2MS), was formed, was unknown. The formation of discrete ion-pairs[3] (Scheme 1), which would give 2MS as the most probable product of Wagner–Meerwein rearrangement,[2] has been previously regarded as a less likely course of gas-phase thermolysis.[4] Two other possible pathways may also be considered.



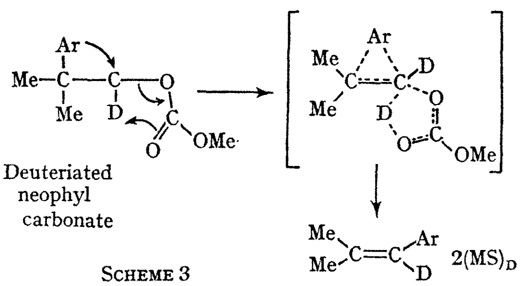
Scheme 1

In one of these (Scheme 2) 2MS arises *via* a high temperature allylic isomerization of the original rearrangement product BP which can be recognized as a 1,3-sigmatropic hydrogen shift.[5] Evidently deuteriation of the BP could reduce the extent of 2MS formation in a thermal reaction, subsequent to the thermolysis of the neophyl ester, in accord with a primary kinetic isotope effect.

The other possibility, a competing five-membered cyclic concerted transition state, involving α-elimination accompanying phenyl migration, could account for the occurrence of the 2MS (Scheme 3). The maximum deuterium isotope effect (k_H/k_D) calculated from the data given by Wiberg[6] for reaction at 575° is 1·88. Thus, if Scheme 3 were operative and the full kinetic isotope effect is to be realized in this transition state, the ratio of unconjugated to conjugated olefin, $(BP)_D/(2MS)_D$, formed from the appropriately deuteriated neophyl carbonate, should be increased by a measurable amount over that obtained in the non-isotopic substrate thermolysis.



Scheme 2



Scheme 3

Experiments designed to distinguish these mechanistic alternatives yielded the following information.

(a) Under suitable reaction conditions[1] (575°) chosen to effect elimination in neophyl carbonate accompanied by little or no cracking, BP is also isomerized to 2MS to the maximum extent of 9·4%. Under these circumstances, nearly 44% of the thermolysis product derived from neophyl carbonate is 2MS. Thus the 1,3-sigmatropic rearrangement[5] of BP is not the only source of 2MS in the thermolysis.

(b) The ratio of BP to 2MS arising from thermolysis of the non-isotopic substrate under identical conditions was found to be 1·28. When this ratio is corrected for the maximum amount of isomerization BP → 2MS) which could have occurred, it becomes 1·62.

(c) An identical thermolysis of isotopic neophyl carbonate (deuteriated in the positions indicated in Scheme 3) yielded olefin rearrangement products in the ratio $(BP)_D/(2MS)_D = 1{\cdot}85$.

(d) Mass-spectral analysis of the $(2MS)_D$ showed that only a minor portion (4·3%) of it is dideuteriated, in accord with the allylic rearrangement depicted in Scheme 2. The reduced percentage of isomerization in the deuteriated olefin could be ascribed to a kinetic isotope effect ($k_H/k_D = 1{\cdot}4$) involved in this process as well. The preponderance of monodeuteriated $(2MS)_D$ in the product (*versus* dideuteriated) substantially corroborates the prediction of Scheme 3.

(e) When corrected for the amount of $(2MS)_D$ formed in the isotopic neophyl carbonate thermolysis *via* secondary isomerization of the $(BP)_D$, the ratio $(BP)_D/(2MS)_D$ becomes 2·41. Thus, the kinetic isotope effect on Scheme 3 is $k_H/k_D = 1{\cdot}5$. This is a significant value at 575°, amounting to nearly 80% of the theoretical maximum, and must, therefore, be deemed a *primary* deuterium isotope effect.[6]

The occurrence of an unusual five-membered cyclic, concerted transition state of α-elimination in gas-phase thermolysis of neophyl esters is made more probable by these data. That thermal isomerization of unconjugated to conjugated olefin competes only poorly with this α-elimination mechanism (as the source of conjugated olefin product) may be regarded as a consequence of the Woodward–Hoffman rules;[5] a 1,3-sigmatropic rearrangement of this nature is symmetry-allowed only *via* a difficult path. The permissible antarafacial 1,3-hydrogen transfer is not apparently well accommodated geometrically and demands some distortion of the π-electron framework.

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[4] H. Kwart and M. T. Waroblak, *J. Amer. Chem. Soc.*, 1967, **89**, 7145.

[5] For a thorough discussion on these reactions, see R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

[6] K. Wiberg, *Chem. Rev.*, 1955, **55**, 713.