Reaction Rates by Flow System Thermolysis; the Competitive Components of the Oxy-Cope Reaction

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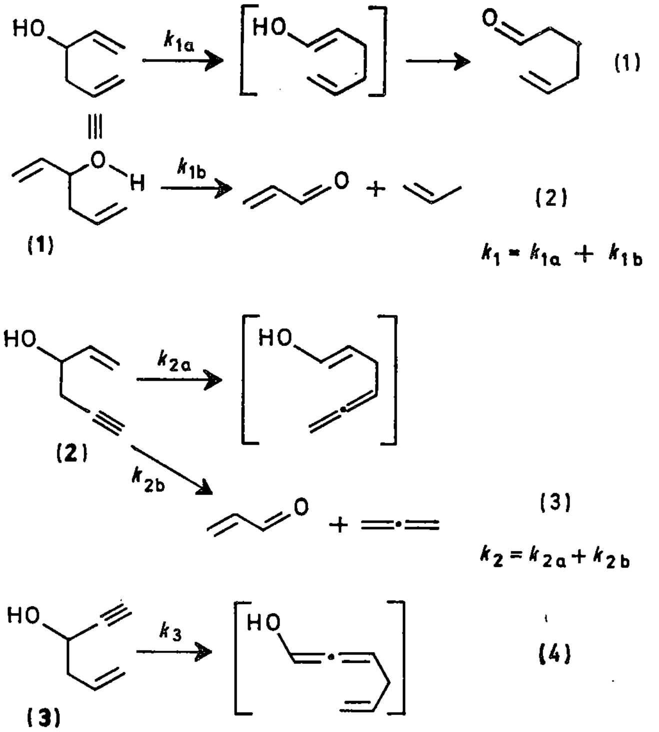
Summary The flow system co-pyrolysis of compounds, one of whose decomposition rates is known, allows the determination of the thermolysis rate of the other component; this technique has been utilized to measure the reaction rates of the individual competitive components of the oxy-Cope as well as the acetylenic oxy-Cope reactions.

THERMOLYSES of hexa-1,5-dien-3-ols, the oxy-Cope reaction, lead to products ascribable to two competing, intramolecular first-order processes, equations (1) and (2). By the Cope process, compound (**1**) gives an enol which subsequently tautomerizes, in the liquid state, to give the observed carbonyl end product. The competing process is a β-hydroxy-olefin cleavage reaction.[1] Individual rate constants for the two competing components of the reaction system have not been reported previously, presumably due to the inherent difficulties in the determination of concentrations in the complex product mixtures. The acetylenic oxy-Cope process of (**2**) is analogous and is further complicated by the subsequent thermal rearrangements of the primary enolic product.[2]



The acetylenic oxy-Cope reaction of (**3**), however, gives only products derived from the primary "allenol" intermediate and no contribution from the corresponding cleavage reaction could be detected. Kinetic parameters for this thermolysis have been reported.[3] The reaction rate of (**3**) appeared to be of the same order of magnitude as those of (**1**) and (**2**).

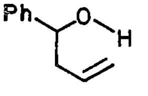
Rate constants for the individual reaction pathways of (**1**) and (**2**) and (**3**) have now been determined at 350° by using an internal standard in a flow system. The co-thermolysis of a mixture of (**1**) and (**3**), under conditions such that some of both substances survives, allows the direct determination† of the ratio of k_1/k_3. Since the product ratio obtained from the thermolysis of (**1**) is readily determined, relative values of k_{1a} and k_{1b} could also be calculated. Similarly, thermolysis of a mixture of (**1**) and (**2**) leads to the ratio of k_1/k_2 and relative values of k_{2a} and k_{2b} could be ascertained from the known thermolysis product ratio[3] of (**2**). Results of thermolyses are summarized in Table 1.

TABLE 1

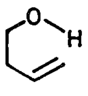
Relative thermolysis rates at 350 °C

	k_{Total}	k_a	k_b
Hexa-1,5-dien-3-ol, (**1**)	1·00	0·60 ± 0·02	0·40 ± 0·02
Hex-1-en-5-yn-3-ol, (**2**)	2·56 ± 0·25	1·53 ± 0·15	1·03 ± 0·10
Hex-5-en-1-yn-3-ol, (**3**)		3·24 ± 0·22	

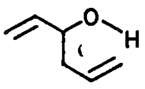
The indicated error limits are based solely on uncertainties of ±2% in each of the g.l.c. areas utilized in the analyses of the co-thermolyses and also represent the maximum error to be anticipated from any single determination. The method is particularly insensitive to small deviations in temperature if two similar reactions are utilized. Thus, a variation in temperature of ±1° during either of the above co-thermolyses would lead to an error of less than 1% in the relative rates, even if the activation energies for either (**1**) or (**2**) varied by 20% from the value of 30 kcal mol^{-1}, previously reported[3] for (**3**).



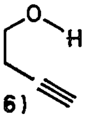
(**4**)



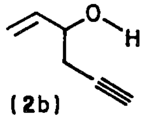
(**5**)



(**1b**)



(**6**)



(**2b**)

The actual rate constants for the above processes were evaluated through the use of 1-phenylbut-3-en-1-ol, (**4**), as an internal standard in the flow system. The choice of (**4**) was predicated on the recent report[4] which indicated its thermolysis rate in the 350° region to be of the same order of magnitude as those anticipated for (**1**), (**2**), and (**3**). The availability of such a rate constant obviated the need for extensive extrapolation from the rates of any of the potential standards[6] which have been reported in substantially lower temperature regions. The co-thermolysis of (**1**) and (**4**) afforded the corresponding rate ratio and hence all the above constants could be evaluated. The results are summarized in Table 2, together with pertinent constants obtained from other sources.

TABLE 2

Rate constants at 350 °C ($k \times 10^3$ s^{-1})

	k_{Total}	k_a	k_b
Hexa-1,5-dien-3-ol, (**1**)	2·0	1·2	0·80
Hex-1-en-5-yn-3-ol, (**2**)	5·1	3·1	2·0
Hex-5-en-1-yn-3-ol, (**3**)	—	6·5	—
1-Phenylbut-3-en-1-ol, (**4**) ..	—	—	1·21(4)
But-3-en-1-ol, (**5**)	—	—	0·063(7)
But-3-yn-1-ol, (**6**)	—	—	0·18(5)

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† The flow system utilized has been described in ref. 1. In the thermolysis of a mixture of (**1**) and (**3**), both compounds are subjected to identical conditions and thus the unknown time factor is cancelled. The equation applicable is $k_1/k_3 = \log(C_1^\circ/C_1)/\log(C_3^\circ/C_3)$.

Runs under various conditions afforded a k_1/k_4 ratio of 1·65 with a mean deviation of 0·13. The latter value is well within the error limits to be expected on the basis of uncertainties of g.l.c. areas.

Internal consistency of the relative rate values is indicated by a comparison of the observed rate enhancements on the two pericyclic reactions. The effect of a vinyl substituent on β-hydroxy-olefin cleavage is rate enhancement by a factor of 12·5 [*e.g.*, compare (**1b**) and (**5**)]. By comparison, in the closely related β-hydroxyacetylene cleavage, (**2b**) reacts at a rate 11 times that of (**6**). These effects are in agreement with those of a substantial number of other substituents on the two reactions.[5]

The accuracy of individual rate constants determined by this method will of course be governed both by that of the standard chosen and by the uncertainties due to the method of analysis utilized. The evaluation of kinetic parameters of oxy-Cope systems by this method will be dealt with in a full paper.

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[3] A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, 1970, **92**, 2404.

[4] G. G. Smith and K. J. Voorhees, *J. Chem. Soc.*, 1970, 2182. The value of this rate constant is in excellent agreement with that of an independent determination in a lower temperature region (ref. 5).

[5] A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Amer. Chem. Soc.*, in the press.

[6] For a compilation of a substantial number of potential internal standards, see "Kinetic Data on Gas Phase Unimolecular Reactions," S. W. Benson and H. E. O'Neal, NSRDS-NBS 21, U.S. Government Printing Office, Washington, D.C.

[7] Extrapolated from the data of G. G. Smith and B. L. Yates, *J. Chem. Soc.*, 1965, 7242.