the cation between the oxygen atoms of the semiquinones is the source of line broadening.[3,5,6]

Typical spectra illustrating these observations are depicted in Figure 1.

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The Kinetic Deuterium Isotope Criterion for Concertedness

Sir:

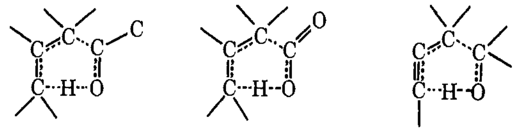
The magnitude of the kinetic, primary deuterium isotope effect has been proposed as a criterion of transition-state structure stemming from theoretical considerations by Westheimer[1] and by Bigeleisen.[2] On the basis of these derivations it is currently presumed that a fully symmetrical transition state will manifest a "maximum" kinetic isotope effect,[3] whereas asymmetric transition states (which are either more product or more reactant-like) will tend to exhibit smaller values of k_H/k_D.

A number of reservations have been expressed as to the applicability of this correlation. Willi and Wolfsberg[4] have suggested that low isotope effects could be a consequence of high hydrogen force constants in the transition state. Bader[5a] has emphasized this occurrence resulting from large antisymmetrical vibrations in a symmetrical transition state.[5b] The presumption that contributions from valency bending forces may be cancelled out by tunneling[6] (or otherwise) represents a further possible limitation. Saunders[7] has developed a model of the transition state for H transfer which suggests that proton coupling with other atomic motions has a significant influence on the isotope effect, a conclusion which is at variance with the very basis of Westheimer's[1] and Bigeleisen's[2] earlier derivations. On the other hand, a model calculation by O'Ferrall and Kouba[8] appears to provide strong support for the correlation of transition-state symmetry and the magnitude of k_H/k_D but *only* for systems where H is transferred from carbon. The claim is made that in the transfer of H from oxygen the bending vibrations in the transition state are too large to be ignored.

The theoretical debate[4-8] over the parameters affecting the kinetic isotope effect has generated remarkably little experimental data which might afford a basis for decision among conflicting claims. Moreover, contemporary interest in concerted reaction mechanisms[9] presents the urgent necessity for a reliable criterion of the symmetrical transition state. Thus, an estimate of the degree of concertedness in cases of sigmatropic hydrogen migration[9] might be realized by measurement of k_H/k_D. Of similar importance is the fact that the magnitude of the primary isotope effect has often been used[10] as an index to transition-state structure in reactions where proton transfer is rate limiting. A recent communication in this journal,[11] however, has challenged the validity of this application.[10d]

We have undertaken the measurement of k_H/k_D as a function of temperature in the thermolysis of three substrates broadly classifiable as β-hydroxyolefins. The members of this series represent significant variation in the nature of the hydroxyl bond, and the hybridization of both the C-1 and the C-4 (terminal carbon) to which H is transferred. Two of these reactions (see Chart I) have been described[12,13] as more or less concerted in nature on the basis of the product formed from the deuterated substrate,[10] and kinetic order and activation parameter[11] criteria. The third case, namely, the thermolytic fragmentation of 3-butyn-1-ol, though no report of previous studies seems to exist, nonetheless proceeds in very similar fashion and is characterized by activation parameters which are nearly identical with those of the other two. Moreover, the very fact that all three reactions show almost the same rates at all temperatures, despite the very considerable range of substituent and structural variation, is of itself a coincidence which strongly suggests a truly concerted, sigmatropic transition state.

Chart I. Transition States for Thermolysis of Various β-Hydroxyolefins



4-penten-2-ol 3-butenoic acid 3-butyn-1-ol

We have also shown that the reaction in each case proceeds with no evident medium dielectric influence on rate, and occurs with equal facility in the gas and liquid phase where wall effects can be considered to be entirely absent. Clearly, therefore, the transfer of hydrogen between the carbon and oxygen termini cannot be attended by any significant degree of charge development on any of the atoms involved in the transition state. The presence of a high concentration of water vapor in all instances exerts no effect on the rate.

Reaction rates were measured in a flow system[14] under circumstances where the substrate was highly diluted with very "dry" helium and passed into a thermostated, gold coil reactor characterized by only negligible wall effects.[12] Several experimental difficulties had to be confronted in measuring k_H/k_D over a large temperature range (*ca.* 100°). For one, the extent of deuteration of the substrate hydroxyl function had

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(1) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(2) J. Bigeleisen, *Pure Appl. Chem.*, **8** (3–4), 217 (1964).

(3) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(4) A. V. Willi and M. Wolfsberg, *Chem. Ind.* (*London*), 2097 (1964).

(5) (a) R. F. W. Bader, *Can. J. Chem.*, **42**, 1822 (1964). (b) The symmetrical transition state is essentially defined by the assumption[2] of a maximum deuterium isotope effect, namely, the arrangement of maximum energy content on the reaction path in which the H vibrations to C and O (C- - -H- - -O) are immobilized; that is to say, the arrangement in which all C⁓H stretching vibrational energy is lost.

(6) R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1965).

(7) W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **91**, 16 (1969).

(8) R. A. M. O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

(9) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2046, 2511 (1965).

(10) A few common examples are: (a) C. G. Swain and E. R. Thornton, *ibid.*, **84**, 817 (1962); (b) K. C. Brown and W. H. Saunders, Jr., *ibid.*, **92**, 4292 (1970); (c) E. R. Thornton, *J. Org. Chem.*, **27**, 1943 (1962); (d) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, *Ser. A*, **294**, 273 (1966).

(11) F. G. Bordwell and W. J. Boyle, Jr., *J. Amer. Chem. Soc.*, **93**, 512 (1971).

(12) R. T. Arnold and G. Smolinsky, *ibid.*, **81**, 6433 (1959); *J. Org. Chem.*, **25**, 129 (1960).

(13) G. G. Smith and B. Y. Yates, *J. Chem. Soc.*, 7242 (1965).

(14) H. Kwart, S. Sarner, and J. Olson, *J. Phys. Chem.*, **73**, 4056 (1969).

to be largely complete, since otherwise a "maximum" k_H/k_D value could not be realized without making undesirable corrections for the presence of the more reactive protio substrate. This condition was achieved to a satisfactory extent by storing the nearly fully deuterated substrate in toluene over 99.5% D_2O and injecting only the D_2O-saturated solution. Moreover, since the H–D exchange occurs very rapidly, each "rate" injection into the helium gas stream was immediately preceded by an injection of D_2O to diminish the possible influence of adventitious water vapor in the flowing gas. Such precautionary measures resulted in an apparently high order of reproducibility and accuracy.

An Arrhenius plot of the data for both protio and deutero substrates (see Table I) over the full temperature range of measurement is presented in the accompanying graphs (see Figure 1). The dotted line drawn through the deutero points traces the theoretical curve of the "maximum" values[3] of k_H/k_D for one stretching vibration of the hydroxyl bond in the respective substrates, *i.e.*, assuming the zero-point energy difference, O–H *vs.* O–D, alone determines the k_H/k_D value. The experimental points and the theoretical line for a fully symmetrical transition state[1,2] are nearly coincident in all instances. The slopes and intercepts (see Table I) of the experimental and theoretical lines are no more than 5% and most often less than 3% apart. In fact, the degree of departure of the deuterated cases from the "theoretical" line in all the plots is no greater than could be expected in view of the problems experienced in achieving total deuteration of the hydroxyl function.

Table I. Experimental and Theoretical Values of the Maximum Deuterium Isotope Effect[e]

Substrate	—Theoretical[a]— −Slope[c]	Intercept[c]	——Obsd[b]—— −Slope[c]	Intercept[d]
4-Penten-2-ol	20.9	26.3	21.4 ± 0.4	27.2 ± 0.5
3-Butenoic acid	19.9	25.3	19.9 ± 0.4	25.4 ± 0.6
3-Butyn-1-ol	21.4	26.9	21.3 ± 0.3	26.7 ± 0.4

[a] Presuming zero-point energy difference (O–H *vs.* O–D) alone determines the rate difference anticipated. [b] Calculated by a regression analysis of all the experimental points displayed in Figure 1. [c] Slope = $-\Delta Ea/R$, for the Arrhenius plots in Figure 1. [d] Intercept = ln A, for the Arrhenius plots. [e] The ΔEa = 40 ± 0.6 kcal/mol and ΔS = −10 ± 1 eu for the nondeuterated substrates.

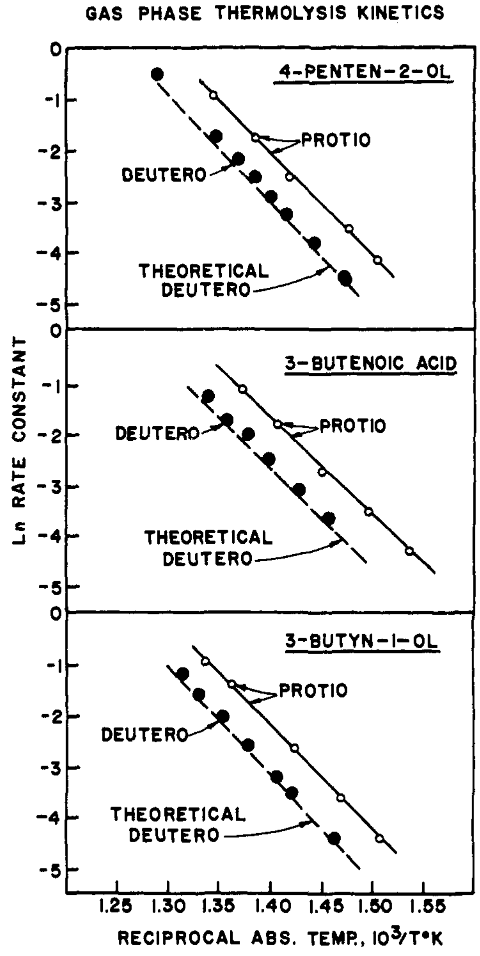

Figure 1.

These results, therefore, appear to answer most doubts and qualifications of the validity of the kinetic deuterium isotope criterion. They confirm the absence of any serious effects arising from change in hybridization and valence geometry of the carbon to which H is transferred. Moreover, the ionic character of the O–H bond and the hybridization of other atoms involved in the cyclic transition state, factors which could also be implicated in tunneling[6] and other causes of the anticipated deviations[4-8] from the Westheimer[1]–Bigeleisen[2] correlation, do not appear to be of primary consequence in determining the k_H/k_D magnitude in concerted H transfer mechanisms.[15] In continuation of these studies, we are presently examining the effects of changing the heteroatom (from oxygen to nitrogen to sulfur) and of a variety of substituents on the transition-state skeleton.

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[15] A referee has contended that the results reported above "... might show that the transition states have different symmetries and that k_H/k_D is insensitive to transition state symmetry." However, in the opinion of the authors, the referee's conclusion is unwarranted in view of the fact that current theory[1,2] of the origin of k_H/k_D was developed from a very clear definition of the symmetrical transition state[5a] and predicts what sensitivity the relationship should show. We propose that there is no evident disparity in the nature of predictions which can be made, respectively, on the basis of a concerted and a symmetrical transition state.

Nucleophilic Alkylidene Transfer Reagents. Synthesis of Spiro Compounds[1]

Sir:

The synthetic value of ylides derived from salts of sulfoximines[2] and anions derived from N-p-toluenesulfonyl sulfoximines,[3] as nucleophilic alkylidene transfer reagents, has previously been recorded. We now

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[1] Part XXX in the series Chemistry of Sulfoxides and Related Compounds.

[2] C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, **90**, 3890 (1968); C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968); C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

[3] C. R. Johnson and G. F. Katekar, *ibid.*, **92**, 5753 (1970).