

## SESSION I

### II. THEORY AND INTERPRETATION OF ISOTOPE EFFECTS

#### (A) General aspects

**Correlation of Kinetic Isotope Effects with Chemical Bonding in Three-centre Reactions**—J. BIGELEISEN, *Brookhaven National Laboratory, U.S.A.*

*Question:* First, does your treatment take tunnelling into account? Secondly, does the occurrence of inverse isotope effects in unsymmetrical transition states, where the total force constant on B is larger than in the initial state, necessarily correspond to intermediate compound formation?  
V. J. SHINER, JR., *Indiana University, U.S.A.*

*Answer:* My study allowed for small tunnelling effects, up to the order of the Wigner correction,  $0(h/kT)^2$ .

An inverse isotope effect in an unsymmetrical transition state does not imply intermediate compound formation. The transition state has a maximum in the energy surface along the reaction co-ordinate, but minima in all other co-ordinates. The intermediate compound has minima in all co-ordinates. If the transition state is unsymmetrical, many cases can be visualized in which the force constant on B will exceed its magnitude in the substrate. Two examples are given in *Figure 1*. BIGELEISEN

*Comment:* Isotope effects on acid-catalysed aromatic hydrogen exchange provide an example of change in isotope effect with changing transition-state structure:

	HA <sub>r</sub>	Relative reactivity	k <sub>H</sub> /k <sub>D</sub>
	C <sub>6</sub> H <sub>6</sub>	1.00	3.5 <sup>a</sup>
	C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub> (F-position)	10 <sup>3</sup>	7.2 <sup>b</sup>
	1,3,5-Trimethoxybenzene	10 <sup>10</sup>	6.7 <sup>c</sup>
	Azulene	10 <sup>12</sup>	5.6 <sup>d</sup>

<sup>a</sup> McLander; <sup>b</sup> Johnson; <sup>c</sup> Kresge; <sup>d</sup> Long.

Anisole seems to have a nearly symmetrical transition state, whereas the transition states of rapidly acting aromatics would be more reactant-like and those of slowly reacting aromatics more product-like. A. J. KRESGE, *Illinois Institute of Technology, U.S.A.*

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*Question:* How does your model apply to organic reactions in which A or C is a polyatomic molecule with vibrations of its own? And how does it

## QUESTIONS AND DISCUSSION

accord with Johnston and Rapp's contention (H. S. Johnston and D. Rapp. *J. Am. Chem. Soc.* **83**, 1, 1961) that, for the classic treatment to apply, the harmonic region in non-linear, non-parabolic barriers must be much larger than the de Broglie wavelength of particle transfer?  
E. A. HALEVI, *Israel Institute of Technology*

*Answer:* My model gives a good approximation for systems of the type you refer to, for the reasons stated in the paper. This is borne out by detailed numerical calculations which are being presented by Wolfsberg and Stern†.

The model applies to the case of a flat top barrier, and for such barriers there is no tunnelling. Very few experimental systems have been found which show evidence of tunnelling; most of them can be adequately represented by using the Wigner tunnel correction, which I have included in my model system. BIGELEISEN

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*Question:* Dr Bigeleisen's calculations relate to a transition state where ABC is linear. To what extent are the conclusions different if ABC is bent? Could the magnitude of the maximum isotope effect (observed in a series of related reactions) provide information on the geometry in a transition state of this kind? V. GOLD, *University of London, England*

*Answer:* It can be seen from the first quantum approximation, for the high-temperature limit, that the only quantities which enter into the isotope effect are  $(v_1/v_2)_L^\ddagger$ , the masses of the isotopic atoms, and their force constants in the substrate and transition state. Geometry is involved only insofar as it affects the force constant. This conclusion is valid at low temperatures also, as can be seen from the reduced partition function ratio,  $s/s'$ . Here again, only vibrational frequencies and their shift on isotope substitution play a rôle and they are determined by the masses and forces. Geometry may have a bearing on the forces, but the results are insensitive to geometry. I would say that isotope effects are not a particularly sensitive tool for the direct study of geometrical or stereochemical configuration. BIGELEISEN

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*Question:* With reference to Dr Gold's question, could information on transition-state geometry be obtained from isotope effects observed on a series of related reactions such as those mentioned by Professor Kresge; e.g. if a series of experiments showed that the maximum isotope effect, for a symmetrical transition state, was significantly less than eight? V. J. SHINER, JR., *Indiana University, U.S.A.*

*Answer:* A series of studies of the type suggested would give valuable information on the changes in transition state with molecular substitution. It

† These proceedings, *Pure Appl. Chem.* **8**, 225, 325 (1964).

might be possible to obtain information on whether the transition state is symmetrical, reactant- or product-like and how it changes with substitution. Values of less than eight for the maximum isotope effect definitely point to asymmetric transition states.

**Validity of Some Approximation Procedures used in the Theoretical Calculation of Isotope Effects**—M. WOLFSBERG and M. J. STERN, *Brookhaven National Laboratory, U.S.A.*

*Question:* In a bimolecular displacement, Bigeleisen treats the central carbon atom as an isolated atom. Bulky groups on this atom will force the transition state out of linearity and probably increase the pending frequency, and force constants associated with bonds to this carbon atom will change, etc. How well does this approximation fit into your exact treatment? E. A. HALEVI, *Institute of Technology, Israel*

*Answer:* Slightly different transition-state geometries generally lead to only slightly different transition-state force-constants, if one is attempting to fit experimental results. The replacement of a bulky central group by one atom is, of course, related to the cut-off procedure which we have discussed. I do not wish, at present, to elaborate on the cut-off procedure for primary isotope effects, which is what you have in mind. However, as pointed out in the paper, one should not "cut off" parts of the molecule which are directly involved in the force-constant changes at the isotopic position. WOLFSBERG

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*Comment:* I believe that complete knowledge of the F-matrix is not required for the evaluation of  $\nu_{1L}/\nu_{2L}$ . Only the configuration (G-matrix) and the reaction path need to be specified in order to make the calculation. E. L. MACKOR, *Koninklijke/Shell-Laboratorium, Netherlands*

*Reply:* If you specify that the reaction co-ordinate, *i.e.* the normal co-ordinate corresponding to the frequency  $\nu_L$ , is  $R = \sum \delta_i q_i$  and that it is fairly isotope-independent, then  $\nu_{2L}^\ddagger/\nu_{2L}^\ddagger = (g_{1RR}/g_{2RR})^{1/2}$ , where the  $g$ 's refer to the diagonal R elements of the respective isotopic G-matrices. Of course, the normal co-ordinates, including the normal co-ordinate corresponding to  $\nu_L$ , will generally depend on both the F-matrix and the G-matrix. If R is required with a certain form, as above, it is usually not too difficult to construct an F-matrix yielding a normal co-ordinate corresponding to the frequency of decomposition. WOLFSBERG

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*Question:* Can the EXC factor be important enough at room temperature to explain  $A_D/A_H$  ratios as large as 2 for a secondary isotope effect involving a single deuterium atom? V. J. SHINER, JR., *Indiana University, U.S.A.*

## QUESTIONS AND DISCUSSION

*Answer:* In primary hydrogen isotope effects, an  $A_D/A_H$  value larger than 2 is improbable, if not impossible, in the absence of tunnelling (see R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, New York, 1959). It is highly unlikely that any reasonable model for what one considers a secondary isotope effect would yield an  $A_D/A_H$  value even close to 2 for mono-deuterium substitution, in the absence of tunnelling. Generally, of course, one would not invoke tunnelling in secondary isotope effects.

Incidentally, I would like to make a plea that, when talking of isotope effects, we should adhere to the nomenclature that has been adopted—however unfortunately—and call  $\nu_{1L}/\nu_{2L}$  the “temperature-independent factor” and find some other expression for the “mass-moment-of-inertia factor”. WOLFSBERG