Relative Tritium–Deuterium Isotope Effects in the Absence of Large Tunneling Factors[1]

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Abstract: Model calculations are used to investigate relative tritium–deuterium kinetic isotope effects and their temperature dependences. It is shown that, in the harmonic approximation and in the absence of large tunneling factors, relative effects, defined as $\mathbf{r} = \ln (k_H/k_T)/\ln (k_H/k_D)$, are generally restricted to the range $1.33 \leqslant \mathbf{r} \leqslant 1.58$, within the temperature interval 20–1000°K, provided that the individual tritium and deuterium effects are themselves reasonably large, in the normal direction ($k_{\text{light}} > k_{\text{heavy}}$), and exhibit "regular" temperature dependences at all temperatures. Overall, however, deviations from this range should not be rare. The extent of deviation usually increases with the degree of irregularity of the temperature dependences (temperature-dependence "anomalies") of the individual tritium and deuterium isotope effects. In addition, inverse isotope effects, even those with regular temperature dependences, will usually exhibit ill-behaved relative isotope effects because of the omnipresence in such cases of higher temperature "inversions," where the signs of $\ln (k_H/k_{D(T)})$ change from negative to positive. The relative isotope effect can start to reflect the presence of an inversion or anomaly in the individual effect(s) several hundred degrees away from the inversion temperature or anomalous region. The results of this study, when combined with the results of previous studies of the temperature dependences of individual isotope effects, indicate that the usual estimates of **r** may be used reliably to calculate deuterium isotope effects from measured tritium effects, or *vice versa*, only with sizable magnitude, pure primary, normal direction individual isotope effects and mixed primary–secondary normal direction individual isotope effects of sufficiently large magnitudes to be principally manifestations of the primary substitutions. Similarly, deviant values of relative tritium–deuterium isotope effects may be used to investigate factors such as quantum mechanical tunneling only under the same conditions. Fortunately, these are the conditions most likely to be involved in a study of tunneling.

The effects of hydrogen isotope substitution on reaction rates have been used in several ways to gain information concerning the existence and extent of quantum mechanical tunneling through potential energy barriers. The two most straightforwardly analyzable kinetic isotope effect phenomena attributed to tunneling are: (i) deviations of relative tritium–deuterium effects, defined as $\ln (k_H/k_T)/\ln (k_H/k_D)$, from certain designated ranges assumed to be limiting in the absence of tunneling and (ii) low values of the empirical Arrhenius preexponential factor A_H/A_D (or A_H/A_T) for deuterium (or tritium) effects. The present study is a theoretical analysis and model calculation evaluation of the first of the above tunneling criteria. The second criterion will be the subject of a subsequent publication.[2]

Analysis of Theoretical Treatments

The theoretical justification for using relative tritium–deuterium isotope effects as evidence for tunneling can be found in three publications,[3–5] all of which essentially start with, and assume the validity of, the statistical thermodynamic treatment of kinetic isotope effects[6,7] in the harmonic approximation, using transition-state theory and ignoring condensation effects and quantized rotational degrees of freedom. We too shall, for the present purposes, assume such validity. Thus, the use of the word "exact" in this paper actually means exact within the above limitations.

The exact expression for an isotopic rate-constant ratio in the absence of tunneling can be written completely in terms of vibrational frequencies as

$$\frac{k_1}{k_2} = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} \frac{\prod_i^{3n-6} \frac{u_{2i}}{u_{1i}}}{\prod_i^{3n^{\ddagger}-7} \frac{u_{2i}^{\ddagger}}{u_{1i}^{\ddagger}}} \frac{\prod^{3n-6} \frac{[1 - \exp(-u_{1i})]}{[1 - \exp(-u_{2i})]}}{\prod^{3n^{\ddagger}-7} \frac{[1 - \exp(-u_{1i}^{\ddagger})]}{[1 - \exp(-u_{2i}^{\ddagger})]}} \times \frac{\exp\left[\sum^{3n-6} (u_{1i} - u_{2i})/2\right]}{\exp\left[\sum^{3n^{\ddagger}-7} (u_{1i}^{\ddagger} - u_{2i}^{\ddagger})/2\right]}$$

$$R_{1/2} = N_{1/2}(\text{VP})_{1/2}(\text{EXC})_{1/2}(\text{ZPE})_{1/2} \qquad (1)$$

where the subscripts 1 and 2 refer to light and heavy isotopic species, respectively; n = the number of atoms; $u_i = h\nu_i/kT$, ν_i = a normal vibrational frequency, h = Planck's constant, k = Boltzmann's constant, and T = absolute temperature; the numerators of VP, EXC, and ZPE refer to the frequencies of the isotopically substituted reactant and the denominators refer to the real (genuine) frequencies of the transition state (‡); $\nu_L^{\ddagger}$ is the transition-state zero or imaginary frequency representing the reaction coordinate. For simplicity, only one isotopically substituted reactant is assumed and the statistical symmetry numbers have been omitted. The practice of referring to R as the "classical isotope effect" because it ignores tunneling is most unfortunate, since such reference obscures the fact that only N is classical; (VP)(EXC)(ZPE) is a purely

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(1) Supported in part by the U. S. Atomic Energy Commission under Contract No. AT (30-1)-3663.

(2) M. E. Schneider and M. J. Stern, manuscript in preparation.

(3) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, 80, 5885 (1958).

(4) J. Bigeleisen, "Tritium in the Physical and Biological Sciences," Vol. 1, International Atomic Energy Agency, Vienna, 1962, p 161.

(5) E. S. Lewis and J. K. Robinson, *J. Amer. Chem. Soc.*, 90, 4337 (1968).

(6) J. Bigeleisen, *J. Chem. Phys.*, 17, 675 (1949).

(7) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 15 (1958).

quantum mechanical contribution.[8] Indeed, at infinite temperature, ZPE = 1 and EXC = 1/VP, so that $R = N$, the classical limit.

Equation 1 can also refer to an isotopic equilibrium constant ratio, with $R_{1/2} \equiv K_1/K_2$, the N term omitted, and the transition-state contributions to VP, EXC, and ZPE replaced by corresponding isotopically substituted product terms taken over all $3n - 6$ frequencies.

We define relative tritium–deuterium isotope effects as follows

$$\mathbf{r} = \ln R_{\mathrm{H/T}}/\ln R_{\mathrm{H/D}}$$

$$\mathbf{n} = \ln N_{\mathrm{H/T}}/\ln N_{\mathrm{H/D}}$$

$$\mathbf{v} = \ln (\mathrm{VP})_{\mathrm{H/T}}/\ln (\mathrm{VP})_{\mathrm{H/D}}$$

$$\mathbf{e} = \ln (\mathrm{EXC})_{\mathrm{H/T}}/\ln (\mathrm{EXC})_{\mathrm{H/D}}$$

$$\mathbf{z} = \ln (\mathrm{ZPE})_{\mathrm{H/T}}/\ln (\mathrm{ZPE})_{\mathrm{H/D}}$$

$\mathbf{n}$, $\mathbf{v}$, and $\mathbf{z}$ are temperature independent, while $\mathbf{r}$ and $\mathbf{e}$ are temperature dependent.

The theoretical development of Swain and coworkers[3] employed a simplified model for a hydrogen-transfer reaction. In the reactant the hydrogen atom of interest is bonded to a very heavy rigid group X; in the transition state the XH stretching force constant is zero and the force constants for two (normal) bending motions of the hydrogen atom are altered from the reactant. Using this model, Swain, *et al.*, derived $\mathbf{z} = 1.442$. The further approximation that $\mathbf{r} \approx 1.442$ is often referred to as the Swain–Schaad equation or Swain–Schaad approximation. Swain, *et al.*, did consider contributions to $\mathbf{r}$ from the excitation (EXC) terms in the same model and derived a temperature-dependent correction factor α in the form $\mathbf{r} = 1.442 + (\ln \alpha/\ln R_{\mathrm{H/D}})$, where $\ln \alpha = 0$ at $T = 0$ and is restricted to the range $-0.098 \leqslant \ln \alpha \leqslant 0.146$ at higher temperatures. They did not, however, consider the temperature-independent VP terms, which increase their *relative* contributions to the R's as the temperature is increased and, as stated above, exactly cancel the corresponding excitation terms at sufficiently high temperature.

From eq 1 and the definitions of the contributing relative effects, we can write

$$\mathbf{r} = \frac{\ln N_{\mathrm{H/D}}}{\ln R_{\mathrm{H/D}}}\mathbf{n} + \frac{\ln (\mathrm{VP})_{\mathrm{H/D}}}{\ln R_{\mathrm{H/D}}}\mathbf{v} + \frac{\ln (\mathrm{EXC})_{\mathrm{H/D}}}{\ln R_{\mathrm{H/D}}}\mathbf{e} + \frac{\ln (\mathrm{ZPE})_{\mathrm{H/D}}}{\ln R_{\mathrm{H/D}}}\mathbf{z} \quad (2)$$

showing that $\mathbf{r}$ is actually a weighted average of the individual contributors. The temperature dependence of $\mathbf{r}$ derives from the temperature dependence of $\mathbf{e}$ and the temperature dependences of the coefficients of each of the contributing relative effects. At high temperatures, as $(\mathrm{EXC})_{\mathrm{H/D}} \rightarrow 1/(\mathrm{VP})_{\mathrm{H/D}}$, $\mathbf{e} \rightarrow \mathbf{v}$ (for the Swain model, $\mathbf{v} = 1.585$) and the contribution of the EXC term to $\mathbf{r}$ is exactly cancelled by the contribution of the VP term. As the temperature is further increased, $(\mathrm{ZPE})_{\mathrm{H/D}} \rightarrow 1$ and $R_{\mathrm{H/D}} \rightarrow N_{\mathrm{H/D}}$ so that the infinite-temperature limit to $\mathbf{r}$ is $\mathbf{n}$. For the Swain model, $\mathbf{n} = 1.585$, corresponding to the ratio of the maximum possible value of $\ln N_{\mathrm{H/T}}$ $(= \ln \sqrt{3})$ to the maximum possible value of $\ln N_{\mathrm{H/D}}$ $(= \ln \sqrt{2})$ for any properly constructed model reaction. It is important to realize, however, that the ratio of these two maximum values is *not* necessarily the maximum possible value of $\mathbf{n}$ for a properly constructed model. The zero-temperature limit to $\mathbf{r}$ can also be deduced from eq 2. As $T \rightarrow 0$, $(\mathrm{EXC})_{\mathrm{H/D}} \rightarrow 1$, $(\mathrm{ZPE})_{\mathrm{H/D}} \rightarrow \pm\infty$, and both $N_{\mathrm{H/D}}$ and $(\mathrm{VP})_{\mathrm{H/D}}$ remain at their temperature-independent values. Thus, the zero-temperature limit to $\mathbf{r}$ is $\mathbf{z}$.

Bigeleisen[4] criticized the theoretical treatment of Swain, *et al.*,[3] because of its neglect of VP contributions and because of the fact that, in the model used, all isotope-dependent frequencies are shifted by factors of exactly $2^{-1/2}$ or $3^{-1/2}$ by deuterium or tritium substitution, respectively, a situation impossible for real molecules according to the Teller–Redlich product rule. Bigeleisen's method of attack was to establish upper and lower limits to $\mathbf{r}$ by considering its low- and high-temperature behavior. He showed, without introducing additional approximations to the exact theory, that the infinite-temperature limit to $\mathbf{r}$ for equilibrium isotope effects is 1.333. The same limit applies to the purely quantum mechanical contributions to kinetic isotope effects $(R_{1/2}/N_{1/2})$[9] *if the Wigner tunneling correction factors are included* $[W = (1 + |u_{1\mathrm{L}}^{\ddagger}|^2/24)/(1 + |u_{2\mathrm{L}}^{\ddagger}|^2/24)$; $u_{\mathrm{L}}^{\ddagger} = h\nu_{\mathrm{L}}^{\ddagger}/kT]$. (More sophisticated tunneling corrections reduce to the Wigner correction at sufficiently high temperature.) Bigeleisen proposed this infinite-temperature limit to $\mathbf{r}$ as the lower limit. However, recent studies of the temperature dependences of both equilibrium[10,11] and kinetic[12] isotope effects have shown that the values of the individual $R_{1/2}$ values at intermediate temperatures need not bear direct relationships to the behavior at the temperature extremes. Thus, the infinite-temperature limit to $\mathbf{r}$ is not necessarily a lower limit.

Bigeleisen established an upper limit of 1.55, for $\mathbf{r}$ for an equilibrium process or $\mathbf{r}_{\mathrm{QM}}$ for a rate process, by considering Swain's value of $\mathbf{z}$ to be an upper limit to $a = \ln [(s_{\mathrm{T}}/s_{\mathrm{H}})f_{\mathrm{H/T}}]/\ln [(s_{\mathrm{D}}/s_{\mathrm{H}})f_{\mathrm{H/D}}]$, where $(s_2/s_1)f_{1/2}$ is the reduced partition-function ratio,[8] and by examining calculated values of $\ln (s_{\mathrm{D}}/s_{\mathrm{H}})f_{\mathrm{H/D}}$ and a for a few diatomic and triatomic molecules. For the complete $\mathbf{r}$ for a rate process, $\mathbf{n}$ must be included. Using a first-order perturbation theory approximation,[13] Bigeleisen found $\mathbf{n}$ to fall in the narrow range 1.56–1.58 for a large range of three-atom hydrogen-transfer-reaction models (excluding those involving hydrogen molecules). Thus, Bigeleisen's proposed range for the relative isotope effect in a rate process, including Wigner tunneling,[9] is $\mathbf{r}^{\mathrm{W}} = 1.33\text{–}1.58$.[14] Bigeleisen pointed out that quantum mechanical tunneling larger than the Wigner term should produce disproportionately large rates for the protium-substituted compounds and thus should

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[8] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[9] The purely quantum mechanical part of the relative isotope effect, $\ln (R_{\mathrm{H/T}}/N_{\mathrm{H/T}})/\ln (R_{\mathrm{H/D}}/N_{\mathrm{H/D}})$ is referred to in this paper as r_{QM}. (For an equilibrium, of course, $\mathrm{r} = \mathrm{r}_{\mathrm{QM}}$.) A prime on R or r is used to denote that tunneling corrections have been included. The prime is replaced by a W when specific reference is made to the Wigner correction. Thus, for example, $\mathrm{r}_{\mathrm{QM}}^{\mathrm{W}}$ refers to the quantum mechanical part of the relative isotope effect with Wigner tunneling corrections included.

[10] M. J. Stern, W. Spindel, and E. U. Monse, *J. Chem. Phys.*, **48**, 2908 (1968).

[11] W. Spindel, M. J. Stern, and E. U. Monse, *ibid.*, **52**, 2022 (1970).

[12] P. C. Vogel and M. J. Stern, *ibid.*, **54**, 779 (1971).

[13] J. Bigeleisen and M. Wolfsberg, *ibid.*, **21**, 1972 (1953); **22**, 1264 (1954). See a discussion of this method in M. J. Stern and M. Wolfsberg, *ibid.*, **46**, 823 (1967).

[14] Bigeleisen's proposed ranges are then $1.33 \leqslant \mathrm{r}^{\mathrm{W}} \leqslant 1.58$ or $1.33 \leqslant \mathrm{r}_{\mathrm{QM}}^{\mathrm{W}} \leqslant 1.55$ for a rate, and $1.33 \leqslant \mathrm{r} = \mathrm{r}_{\mathrm{QM}} \leqslant 1.55$ for an equilibrium.

lower the observed ln (k_H/k_T)/ln (k_H/k_D) values from "normal."

Finally, Lewis and Robinson,[5] who accepted the Swain–Schaad approximation of $\mathbf{r} \approx 1.442$, showed that tunneling corrections need not produce significant deviations of the relative isotope effect. Generalizing their considerations in the present notation, we include a tunneling correction factor T in eq 1.

$$R_{1/2}' = R_{1/2}T_{1/2} \tag{3}$$

Equation 2 then becomes

$$\mathbf{r}' = \frac{(\ln R_{H/D})\mathbf{r} + (\ln T_{H/D})\mathrm{t}}{\ln R_{H/D}'} \tag{4a}$$

$$\mathbf{r}' = \mathbf{r} + \frac{\ln T_{H/D}}{\ln R_{H/D}'}(\mathrm{t} - \mathbf{r}) \tag{4b}$$

where $\mathrm{t} \equiv \ln T_{H/T}/\ln T_{H/D}$. We see from eq 4a that the tunneling correction simply adds an additional term into the average and from eq 4b that $\mathbf{r}'$ will differ significantly from $\mathbf{r}$ only if t is significantly different from $\mathbf{r}$ and if the tunneling term ln $T_{H/D}$ is an appreciable fraction of the total isotope effect ln R'. Using the approximation $\nu_{HL}^{\ddagger} = \sqrt{2}\nu_{DL}^{\ddagger} = \sqrt{3}\nu_{TL}^{\ddagger}$, Lewis and Robinson calculated, for tunneling factors larger than the Wigner correction, t values significantly lower than 1.333, the value of t generally, although not necessarily, decreasing with increasing $|u_L^{\ddagger}| = h|\nu_L^{\ddagger}|/kT$ and with increasing barrier height. On the other hand, the Wigner correction for the same model increases monotonically from its infinite-temperature ($|u_L^{\ddagger}| = 0$) limit of t = 1.333 to its zero-temperature ($|u_L^{\ddagger}| = \infty$) limit of t = 1.585.

It should be noted that the application of the Wigner correction W does not alter the relative isotope effect zero-temperature and infinite-temperature limits of $\mathbf{z}$ and $\mathbf{n}$, respectively, because

$$\lim_{T\to 0} \frac{\ln W_{1/2}}{\ln (\mathrm{ZPE})_{1/2}} = 0$$

and

$$\lim_{T\to\infty} \ln W = 0$$

Except for Bigeleisen's infinite-temperature limit of 1.333,[15] all of the values and limits for relative tritium–deuterium isotope effects obtained previously[3–5] involve approximations in addition to those inherent in eq 1 and/or correspond to models not strictly obeying relationships inherent in the derivation of eq 1. That is, they do not correspond to what we have defined as "exact" calculations. Nevertheless, the value $\mathbf{r} = 1.442$ has been used extensively for estimating either tritium or deuterium isotope effects from measured values of the other, and deviations from either 1.442 or the 1.33–1.58 range have been taken as evidence for significant tunneling factors.[16] Even large *positive* deviations from these proposed relative isotope effect values have been considered as evidence for tunneling,[17] although there is apparently no theoretical justification for such an interpretation.

To our knowledge, the only previously published test of the previous theoretical treatments based on exact model calculations is that of More O'Ferrall and Kouba.[18] These workers found deviations from the Swain–Schaad approximation of only 2% with model calculations of hydrogen-transfer reactions at 25°C, even though substantial tunneling corrections were included. That study, however, was restricted to linear four- and five-atom transition-state models in which the nonhydrogenic bonds were treated as rigid to stretching motion.[19] The strict linearity of the models makes them, in some respects, similar to the model originally used by Swain, *et al.*, in deriving[3] their relationship.

Model Calculations

Our exact model calculation study of the temperature dependences of kinetic isotope effects[12] provides a large number of test cases for examining the range of $\mathbf{r}$ values to be expected in real reactions. In that study, we investigated the kinetic isotope effects, in the harmonic approximation over the temperature range 20–2000°K, corresponding to several hundred isotopic reaction pair models centering about five basic reaction types of differing degrees of complexity: (i) unimolecular substitution ($\mathrm{S_N1}$) of ethyl-X (X is an "atom" with atomic mass 80, representative of halogen or any heavy group[20]); (ii) bimolecular substitution ($\mathrm{S_N2}$) of ethyl–X with another X atom; (iii) hydrogen transfer between ethane and trifluoromethyl radical; (iv) decarboxylation of malonic acid; and (v) bimolecular β-hydrogen elimination (E2) from *sec*-butyl–X with amide ion. Although the models were not intended to represent faithfully specific real reaction systems, the range of force constant changes between reactants and transition states imposed at the isotopic positions encompasses a large fraction of the entire range of such changes that might be postulated as occurring at hydrogen atoms in any reaction. In the present paper we examine the relative tritium–deuterium isotope effects of the 154 sets[21] of exactly corresponding tritium- and deuterium-substituted model reactions from the earlier study.[12] Twenty-six additional sets, not included in the original collection, were generated for purposes of the present study. Finally, for comparison of rates and equi-

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[15] The infinite-temperature limit $\mathrm{r_{QM}}^W = 1.333$ for a rate applies even to reactions with completely flat potential barriers ($\nu_L^{\ddagger} = 0$), despite the fact that the Wigner corrections for such cases are nil ($\mathrm{r_{QM}}^W = \mathrm{r_{QM}}$).

[16] See, for pertinent references: (a) ref 5; (b) J. R. Jones, *Trans. Faraday Soc.*, **65**, 2138 (1969).

[17] J. R. Jones, *ibid.*, **61**, 95 (1965), measured ln $R_{H/T}$/ln $R_{H/D}$ = 1.84 for the proton transfer from acetone to hydroxide ion in the room-temperature region, and suggested that this high value could be indicative of tunneling. In a later publication (ref 16b), Jones corrected this value by allowing for a statistical correction as well as a secondary isotope effect. His revised value is 1.12 at 20°C.

[18] R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

[19] More O'Ferrall and Kouba's models are similar to the cutoff models proposed by Stern and Wolfsberg[20] but do not completely satisfy the conditions for "proper" cutoff models. However, it is not immediately obvious whether or not the sensitivity of the *relative* isotope effects to the details of a model is such that a proper cutoff model is required for valid conclusions to be drawn. More O'Ferrall and Kouba also carried out some calculations with nonlinear, unbranched, six-atom transition-state models in which all bonds were treated as nonrigid. (These models still fall somewhat short of satisfying the conditions for proper cutoff.) It is not clear from their presentation whether relative tritium–deuterium isotope effects were calculated for these models.

[20] M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 4105 (1966).

[21] In this paper, "set" refers to a deuterium isotope effect case with its corresponding tritium isotope effect case. As before,[12] "case" refers to a unique *F*-matrix (force constants) and *G*-matrix (geometry and atomic masses) combination. Thus, corresponding tunneling-corrected and -uncorrected calculations do not constitute separate cases or separate sets.

libria, 66 sets of relative tritium–deuterium equilibrium isotope effects, based on previous deuterium effect calculations,[11] are considered.

When a specific model is used for illustration, it is identified according to its general reaction type (written for the deuterium-substitution reaction) and sufficient information is given, in parentheses, to allow the details of the calculation (molecular structures, force constants, etc.) to be found in ref 12.

Results and Discussion

Even before examining the actual relative isotope effect results, we can make an important prediction based on the results of the temperature-dependence study.[12] In that study it was shown that kinetic isotope effects can, not uncommonly, go through inversions with varying temperature.[22] For an inverse isotope effect ($k_1 < k_2$), such an inversion must occur at some finite temperature, even if $\ln R_{1/2}$ itself proceeds smoothly and monotonically from its (negative) zero-temperature limit of $\ln (\mathrm{ZPE})_{1/2}$ to its (positive) infinite-temperature limit of $\ln N_{1/2}$. Deuterium and corresponding tritium effects do not exhibit exactly the same inversion temperatures. Thus, at the deuterium inversion temperature **r** will have a pole ($\mathbf{r} = \pm \infty$) and at the tritium inversion temperature **r** will equal zero. The tritium inversion temperature can be either higher or lower than the corresponding deuterium inversion temperature; both types of situations were observed in the present work. Figure 1 shows a few examples of **r** *vs.* log T plots for isotope effects exhibiting inversions but not what we have previously called[12] temperature-dependence "anomalies" (*i.e.*, they exhibit type −A temperature behavior[23]).

When, in addition to simple inversions, $R_{1/2}$ has associated with it anomalous temperature behavior (inflections, extrema, and/or crossovers), the **r** *vs.* log T curve can exhibit extensive "structure," with the **r** values often falling well outside the 1.33–1.58 range at temperatures very far removed from the inversion temperatures. Figure 2 shows several examples of such sets.

It has been shown[12] that deuterium and corresponding tritium isotope effects can even exhibit different temperature-dependence types, although such situations should be rather rare. In such a situation, if either the deuterium or tritium effect exhibits an inversion and the other does not, the behavior of **r** as a function of temperature can be extremely confusing.

Figure 3 shows the **r** *vs.* log T behavior for two particularly interesting sets. The deuterium effect in Figure 3a is of type L, while the corresponding tritium effect is of type −K with the crossover and inversion temperatures below 20°K. The relative isotope effect increases monotonically throughout the 20–2000°K range (zero-temperature limit of $\mathbf{z} = -2.92$, infinite-temperature limit of $\mathbf{n} = 1.75$), passing through the 1.33–1.58 range at intermediate temperatures (~75 to ~ 625°K). The corresponding Wigner-corrected $\ln R_{1/2}$ *vs.* log T plots are of type B and type −D for deuterium and tritium, respectively. The $\mathbf{r}^{\mathrm{W}}$ *vs.* log T curve is similar to the uncorrected **r** *vs.* log T curve. The example shown as Figure 3b represents Wigner-corrected cases with type −C temperature behavior. Although neither the deuterium nor corresponding tritium effect exhibits a crossover, in each case, owing to the maximum and minimum, $R_{1/2} = 0$ is achieved three times in the 20–2000°K range. The resulting $\mathbf{r}^{\mathrm{W}}$ *vs.* log T plot is complex, to say the least.

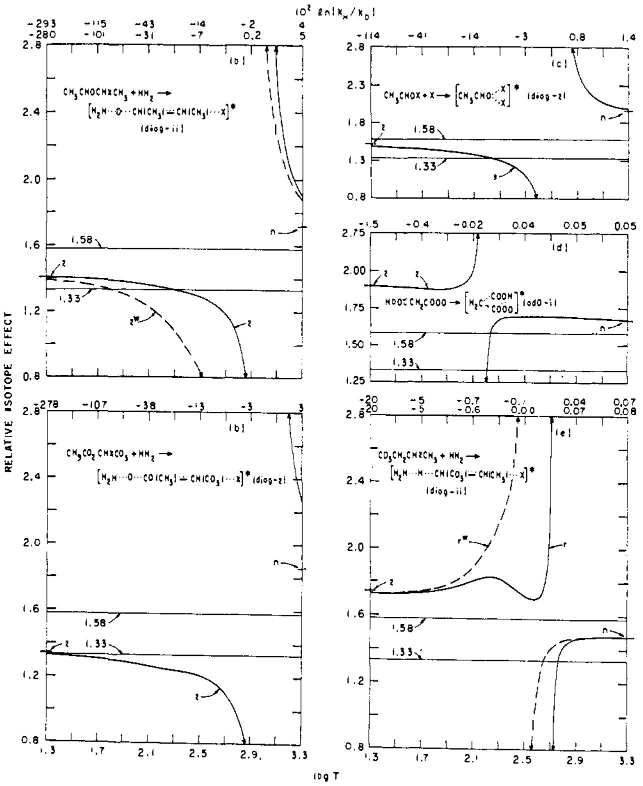

Figure 1. Typical relative tritium–deuterium isotope effects for individual D and T cases exhibiting inversions but otherwise smooth monotonic temperature dependences [(d) and (e) represent no-force-constant-change-like (nfcc-like) isotope effects]. In this and succeeding figures, the abscissas are linear in log T [values given at bottom of lowermost graph(s)]. The abscissa values given at the top of each graph are the values of $\ln (k_{\mathrm{H}}/k_{\mathrm{D}})$ at the relevant temperatures. When a single set of $\ln (k_{\mathrm{H}}/k_{\mathrm{D}})$ values is given, tunneling corrections are not included; when two sets are given, the bottom set includes Wigner tunneling corrections. Solid lines do not include tunneling corrections (r or r_{QM}) and dashed lines include Wigner tunneling corrections (r^{W} or $\mathrm{r}_{\mathrm{QM}}{}^{\mathrm{W}}$). Arrowheads at the ends of line segments indicate poles.

Although the results discussed so far are not for the most common cases, it is clear from these results that *transition-state theory imposes no limits whatsoever on the values of* **r**. Further, the above analysis for inversions applies as well to crossovers, if **r** is replaced with $\mathbf{r}_{\mathrm{QM}}$ (experimentally measurable for equilibria but not for rates).

Portions of some of the curves shown in Figures 1–3 are shaped exactly as one might predict for large tun-

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(22) In this paper, we use the word "inversion" for the experimentally significant situation where $\ln R_{1/2}$ reverses sign and the word "crossover" for the more theoretically significant situation where $\ln R_{1/2}$ reverses direction with respect to $\ln N_{1/2}$. At the inversion temperature, $\ln R_{1/2} = 0$; at the crossover temperature, $\ln R_{1/2} = \ln N_{1/2}$. For equilibria, of course, the two situations are identical.

(23) "Type" describes the general shape of a $\ln R_{1/2}$ *vs.* log T plot.[10–12] Specific types mentioned in this paper are: type A, smooth monotonic; type B, monotonic with one inflection region; type C, minimum and maximum without crossover; type D, single crossover; type E, single crossover with lower temperature inflection region; type H, single crossover with lower temperature minimum and maximum; type I, single crossover with higher temperature maximum and minimum; type K, single crossover with higher temperature inflection region; type L, monotonic with two inflection regions. A minus sign in front of the type letter, *e.g.*, type −A, indicates that at $T \rightarrow 0$ the isotope effect is inverse ($k_1 < k_2$; $\ln R_{1/2} < 0$). The various types are depicted graphically in ref 12.

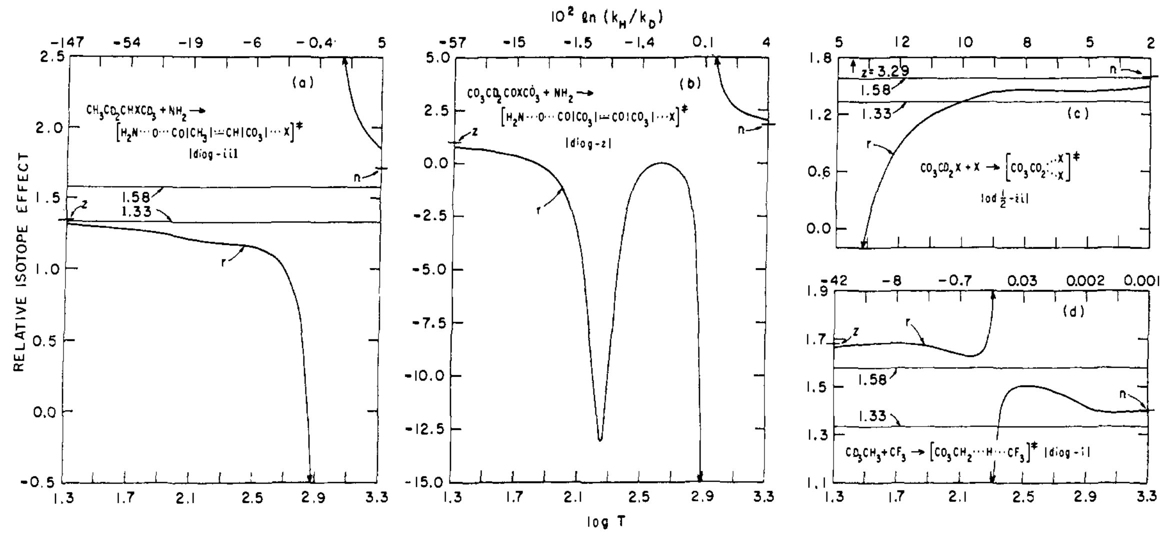

Figure 2. Typical relative tritium–deuterium isotope effects for individual D and T cases exhibiting inversions and temperature-dependence anomalies [(d) represents nfcc-like isotope effects].

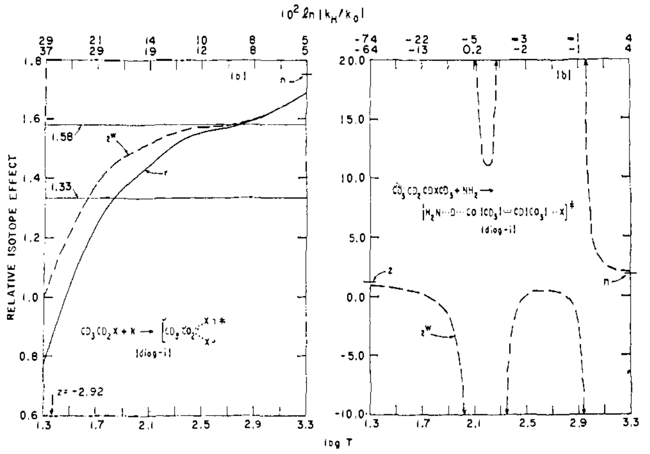

Figure 3. Atypical relative tritium–deuterium isotope effects.

neling corrections (*i.e.*, a sharp decrease in **r** with decreasing temperature) despite the fact that no tunneling corrections or only Wigner corrections were included in the calculations. Even when the strange **r** *vs.* log T behavior is due to simple inversions of the individual $R_{1/2}$'s, **r** can deviate from the 1.33–1.58 range several hundred degrees removed from the inversion temperatures, 500° removed not being unusual. It is apparent that, if inversions occur, serious errors can result from attempting to interpret the observed ln (k_H/k_T)/ln (k_H/k_D) values in terms of tunneling. Experiments can seldom be carried out over more than a 100° range. While one can be wary of an inverse kinetic isotope effect, since such an effect must always be accompanied by a higher temperature inversion, an inversion situation is likely to be overlooked in a case where, in the experimental range, the isotope effect is normal ($k_1 > k_2$). We have found no way of detecting crossovers and other types of temperature-dependence anomalies by examining data over a temperature range removed from the anomalous region.[12] Similarly, we know of no way to detect an inversion from examining *normal* isotope effect data over a temperature range removed from the inversion point.

We now consider cases which do not exhibit inversions, but do exhibit crossovers. Such cases are usually associated with very small quantum effects, since in order for a situation of this nature to obtain, the minimum value of $R_{1/2}$ must fall in the range $N_{1/2} > R_{1/2} > 0$. Thus, the resulting $\mathbf{r}_{QM}$ has a pole, but **r** does not. In the present series of calculations, four such sets were observed for models in which negligible or nil force constant changes between reactant and transition state were imposed at the isotopic positions (nfcc-like isotope effects[24,25]). The isotope effects are of type D in three of these sets and of type E in the fourth. The **r** *vs.* log T curves are shown in Figures 4a–d. Depending on the values of the temperature extreme limits, **z** and **n**, and on the magnitudes of the individual $R_{1/2}/N_{1/2}$ values, the **r** *vs.* log T curve can be almost temperature independent (Figures 4a and 4b) or can have considerable structure and extend both above and below the 1.33–1.58 range (Figures 4c and 4d). We also had in our collection two sets with type E behavior without inversions for models in which significant force constant changes were imposed at the isotopic positions (both primary and secondary positions substituted simultaneously). Figure 4e represents one of these sets. We see that **r** varies greatly over the entire temperature range, exhibits a maximum value of ~3, and is above the 1.33–1.58 range at all temperatures. The Wigner corrections here serve to lower the maximum significantly.

Isotope effect temperature-dependence anomalies need not be associated with inversions or crossovers. In the present series of calculations, such anomalies appeared as inflections in the ln $R_{1/2}$ *vs.* log T plots (type B curves) in five sets of model calculations corresponding (more or less) to α-D_1(-T_1) and α-D_2(-T_2) substitution in a hydrogen-transfer reaction. All of these

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(24) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 2618 (1966).

(25) In a true nfcc (no force constant change) isotope effect, the first quantum correction (including the Wigner tunneling correction) is nil. Although *exactly* nil first quantum corrections cannot obtain in real reactions, model calculations of such situations can provide important information as limiting cases.[24,26,27]

(26) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 225 (1964).

(27) M. Wolfsberg and M. J. Stern, *ibid.*, **8**, 325 (1964).

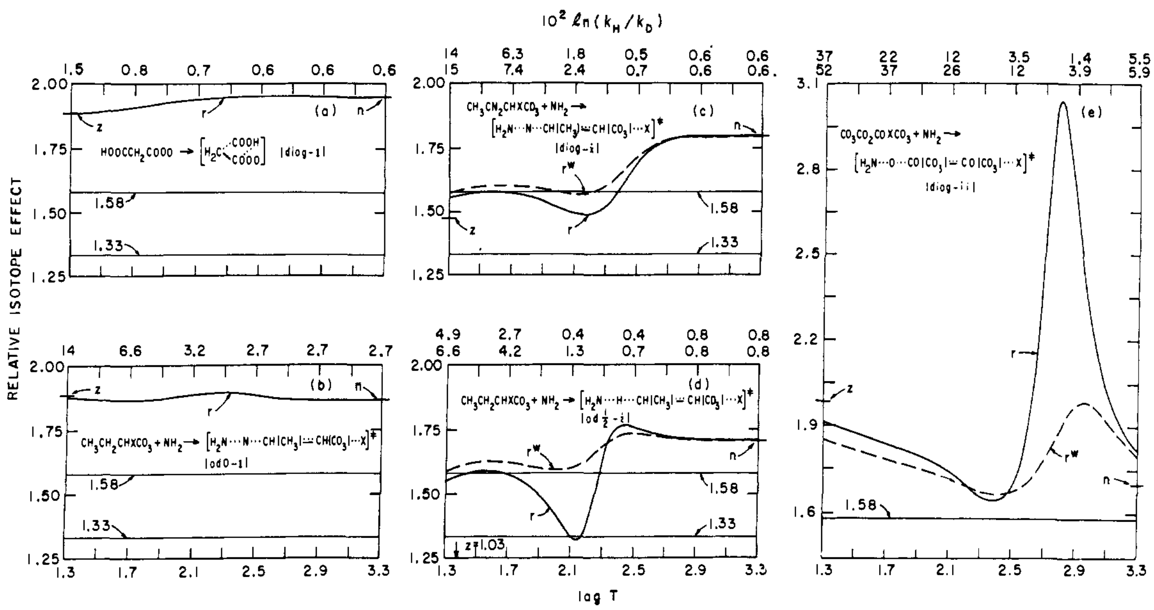

Figure 4. Relative tritium–deuterium isotope effects for individual D and T cases exhibiting crossovers but not inversions. (a)–(d) represent nfcc-like isotope effects, while (e) represents effects due to significant force constant changes. The individual isotope effects are of type D in (a)–(c) and of type E in (d) and (e) [in (c), the individual Wigner-corrected effects are of type A].

cases involve significant force constant changes at the isotopic position(s). (We found several additional examples of type B behavior, but have excluded them from consideration here because either they are associated with inverse effects and thus with inversions, or only the deuterium effects are of type B, the corresponding tritium effects exhibiting different types of anomalous temperature behavior.) Inflections in ln $R_{1/2}$ *vs.* log T behavior would usually be extremely difficult to detect experimentally. The **r** *vs.* log T curves for these five cases all have the same general shape; an example is shown in Figure 5. The values of $N_{1/2}$ are so close to unity in these cases that the **r** and corresponding $\mathbf{r}_{QM}$ curves are practically superimposed up to 2000°K, and the Wigner tunneling corrections make negligible contributions even when the model produces large imaginary $\nu_L{}^{\ddagger}$ values. The **r** values range from $\sim$0.7 to $\sim$1.0 at 20°K (**z** ranges from 0.08 to 0.70), increase to 1.33 at $\sim$125°K, continue to maximum values of $\sim$1.38 at $\sim$250°K, and decrease to $\sim$1.34 at 2000°K. Because of the small $N_{1/2}$ contributions, the values of **r** at 2000°K are still far from their infinite-temperature limits **n**, which ranged, in these cases, from 1.45 to 1.98. When **n** is particularly high, as in the example shown in Figure 5, the curve appears to be turning upward at the highest temperatures.

The importance of these cases is that the **r** *vs.* log T behavior is exactly what one would expect from previous work[3–5] for large tunneling contributions. Yet, this behavior is exhibited in the absence of tunneling and, further, for cases with isotope effect temperature-dependence anomalies which would be unlikely to be detected experimentally.

We have reserved until last a discussion of the relative tritium–deuterium isotope effects for the most common cases, where $R_{1/2}$ is normal and exhibits regular (nonanomalous; type A) temperature behavior. The ln $R_{1/2}$ *vs.* log T curves for such cases decrease smoothly and monotonically, without inflections, from their zero-temperature limits of ln $(ZPE)_{1/2}$ to their infinite-temperature limits of ln $N_{1/2}$. In our kinetic isotope effect calculations,[12] pure primary hydrogen isotope effects of *sizable magnitudes* exhibited only regular temperature behavior. Although we did not investigate[12] a sufficient number of relevant model reactions to allow us to conclude that temperature-dependence anomalies should be extremely rare for normal-magnitude primary hydrogen isotope effects, later work[2] supports this conjecture. We emphasize, however, that we are referring here to *pure primary* isotope effects of *sizable magnitudes.* Cases where isotopic substitutions are made simultaneously at primary and secondary atomic positions are prone to be associated with temperature-dependence anomalies, especially when the force constant changes at the relevant positions are of differing signs. Also, we have observed anomalies in low-magnitude pure pri-

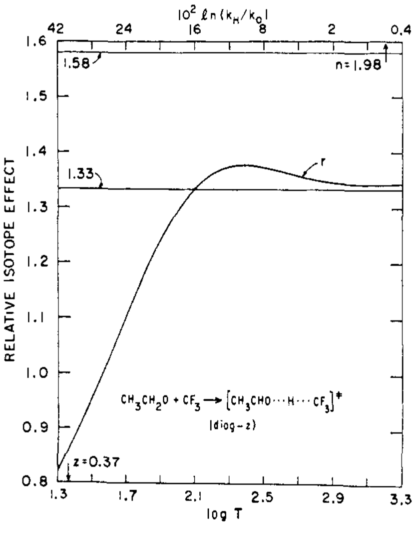

Figure 5. Typical relative tritium–deuterium isotope effect curve for individual D and T cases exhibiting type B temperature dependences.

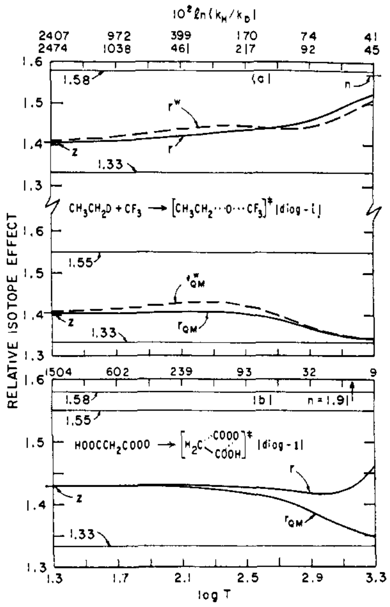

Figure 6. Typical relative tritium–deuterium isotope effects for pure primary hydrogen substitutions.

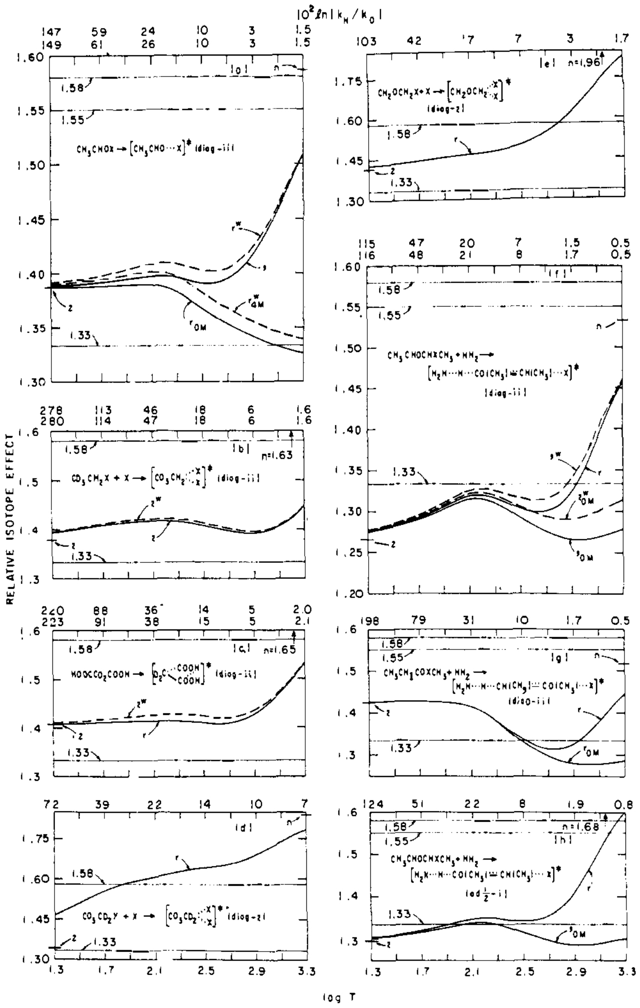

Figure 7. Relative tritium–deuterium isotope effects for pure secondary hydrogen substitutions at atomic positions involved in significant force constant changes, with the individual D and T isotope effects exhibiting regular (type A) temperature dependences.

mary effects in models with abundant force constant changes of differing signs.[28]

Since actual reaction primary hydrogen isotope effects are where one would be most likely to be looking for, or investigating the extent of, quantum mechanical tunneling, the type A model reaction cases are the most significant ones for investigation here. In the following discussion we separate the sets involving type A cases into categories of (i) pure primary effects, (ii) pure secondary effects involving significant force constant changes, (iii) pure secondary nfcc-like effects, (iv) mixed primary and secondary effects, and (v) intramolecular effects.

Eight sets of pure primary isotope effects (from our original collection[12]) exhibiting type A temperature behavior were investigated. Four of these were for models of a hydrogen-transfer reaction and four for models of a decarboxylation reaction. The force constant changes at the isotopic positions are quite varied among the eight sets, as are the potential barrier shapes and reaction coordinates. Nevertheless, the **r** *vs.* log T curves for these sets were quite similar and well behaved, **r** increasing from 1.40–1.43 at 20°K (**z** = 1.40–1.43) to 1.46–1.53 at 2000°K (**n** = 1.58–1.91). As expected,[4,5] the Wigner corrections generally tended to raise **r** slightly at 20°K and lower it slightly at 2000°K. Two examples are shown in Figure 6. Although the increase in **r** from 20 to 2000°K is not necessarily monotonic, the "structure" is minor when considered on an absolute basis. On a relative basis, however, the degree of structure can be quite sensitive to the inclusion of Wigner corrections.

It is not surprising that, for primary hydrogen isotope effects where the most important isotope-dependent frequencies are high lying, the values of **r** at 20°K are very close to the corresponding values of **z**, while the values of **r** at 2000°K can be quite far from the corresponding values of **n**, especially when **n** is high (as in Figure 6b).

Forty-nine sets of pure secondary hydrogen isotope effects involving significant force constant changes and exhibiting type A behavior were examined. Many of the **r** *vs.* log T plots are quite well behaved; some examples are shown in Figure 7a–c. These curves resemble the primary effect curves shown in Figure 6 fairly closely.

The **r** values at 20 and at 2000°K for the pure secondary substitutions are considerably more variable than for the (few) pure primary substitutions discussed above. The values of **r** at 20°K vary from 1.28 to 1.48, with a slight trend toward lower values as the potential energy barrier in the model is made sharper. Although the values of **r** at 20°K are usually in close agreement with their corresponding **z** values (**z** varies from 1.27 to 1.48), in many cases the agreement is fairly poor (deviations up to 0.12 units in **r**). The values of r at 2000°K vary from 1.43 to 1.87, with a distinct trend toward lower values as the potential barrier in the model is made sharper. The corresponding **n** values vary from 1.52 to 1.97. In a secondary isotope effect, ln $N_{1/2}$ is usually an appreciable fraction of ln $R_{1/2}$. Thus, **n** can become important in determining the value of **r** at lower temperatures than it does in primary isotope effects.

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[28] M. J. Stern, M. E. Schneider, and P. C. Vogel, *J. Chem. Phys.*, in press.

Because of the variation in **z** and **n**, and consequently in the values of **r** at the temperature extremes, many of the **r** *vs.* log T curves for the pure secondary isotope effects were outside the 1.33–1.58 range over certain temperature intervals. Let us first consider positive deviations (**r** > 1.58). These will occur at some finite temperature whenever **n** is greater than 1.58. In our model calculations **r** usually became greater than 1.58 above 1000°K. This **r** = 1.58 temperature is lower when a high **n** value is associated with small quantum effects, a situation which could obtain, for example, when small or compensating force constant changes occur in a reaction with a fairly flat potential barrier. Figure 7d shows the **r** *vs.* log T curve for the worst set encountered, in which **r** becomes greater than 1.58 at ~70°K. This curve is unique, however. The more typical "bad" sets had **r** = 1.58 temperatures around 600°K. An example of such is shown in Figure 7e. The individual isotope effects for this set are still experimentally significant at the **r** = 1.58 temperature ($\ln R_{H/D} = 0.038$ at 600°K; $\ln N_{H/D} = 0.013$).

It is unlikely that the positive deviations discussed above would present problems, because of the high temperatures usually involved. Of greater concern are the negative deviations (**r** < 1.33), which occur at low and intermediate temperatures. Negative deviations were observed in only four sets, corresponding to α-D(-T) substitutions in models for a β-elimination reaction with extremely complicated reaction coordinates.[12] The relative isotope effect curves for the worst set are shown in Figure 7f. Here **r** stays below 1.33 until ~850°K (~750° with Wigner tunneling), the minimum value of **r** = 1.28 appearing at the low-temperature (20°K) extreme. We see that the low values of **r** are due to the low values of $\mathbf{r}_{QM}$, which is not restricted to the >1.33 range even with the inclusion of Wigner tunneling corrections. Figure 7g represents a set where the $\mathbf{r}_{QM}$ and corresponding **r** curves do not dip below 1.33 until the intermediate-temperature range (~300°K). This intermediate-temperature negative deviation of $\mathbf{r}_{QM}$ was, in fact, observed in all ten of the β-elimination secondary isotope effect sets in this group, but in six of the sets was overridden by the **n** contribution so that **r** remained above 1.33. Figure 7h shows the **r** behavior for one of the two sets exhibiting both negative and positive deviations within the 20–2000°K temperature range. The final set exhibiting a negative deviation is similar to that shown in Figure 7h, but with a smaller negative deviation and a larger positive deviation. It is clear from these results that neither **r** nor $\mathbf{r}_{QM}$ (nor $\mathbf{r}^{W}$ nor $\mathbf{r}_{QM}{}^{W}$) is restricted to the >1.33 range, even for isotope effects themselves exhibiting nonanomalous temperature behavior. However, we must recognize that the negative deviations for these type A cases only occurred with very complicated models and that they were not excessively large. The minimum values observed in our calculations for both **r** and $\mathbf{r}_{QM}$ were ~1.27.

Nine sets of nfcc-like effects exhibiting type A temperature behavior were investigated. All of these were for flat barriers ($\nu_L{}^{\ddagger} = 0$). The **r** *vs.* log T curves were all very similar, proceeding from relatively high values of 1.72–1.82 at 20°K (**z** = 1.70–1.83), in a more-or-less monotonic sigmoid fashion, to even higher values of **n** (1.87–1.95), which were achieved very closely at relatively low temperatures. The values of **r** were above the 1.33–1.58 range throughout the 20–2000°K temperature range investigated. The two examples shown in Figure 8 illustrate the extremes of the structure of these curves. One additional set of nfcc-like effects, corresponding to a model with a potential barrier of intermediate sharpness ($\nu_{1L}{}^{\ddagger} = 435i$ cm^{-1}), exhibited a crossover (type D) in the absence of tunneling corrections, which was washed out by the Wigner corrections. The $\mathbf{r}^{W}$ *vs.* log T plot for this set has already been exhibited in Figure 4c. $\mathbf{r}^{W}$ oscillates between ~1.58 and ~1.61 in the 20–200°K range (**z** = 1.48) before proceeding upward to **n** = 1.80.

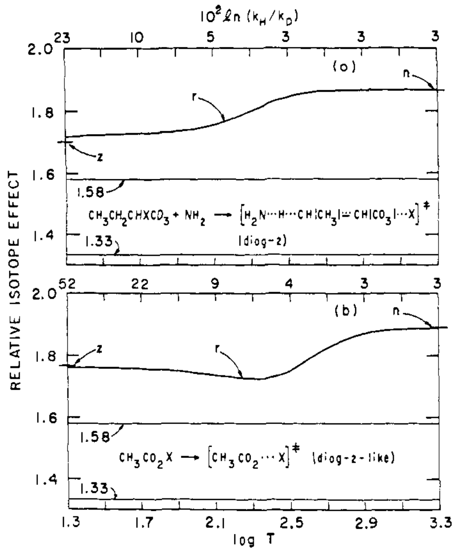

Figure 8. Typical relative tritium–deuterium isotope effect curves for individual D and T nfcc-like isotope effects exhibiting regular (type A) temperature dependences.

Twenty-eight sets of mixed primary and secondary effects exhibiting type A temperature behavior were investigated.[29] The **r** *vs.* log T curves were all very similar to the corresponding pure primary effect curves, except that the values of **r** were generally very slightly higher over certain temperature intervals, but still well within the 1.33–1.58 range. This almost complete overriding of the secondary effects by the primary effects existed even when the secondary effects were by themselves of opposite sign to the primary effects and/or exhibited anomalous temperature behavior with corresponding **r** *vs.* log T curves well outside the 1.33–1.58 range.

Another type of mixed primary–secondary isotope effect is an intramolecular effect. Here, the reactant is identical for the two isotopic reactions, but the position of isotopy is different in the transition state, in one case being at the primary position and in the other at a secondary position. Eight sets of intramolecular isotope effects exhibiting type A temperature dependences were investigated,[29] corresponding respectively to the pure primary effects discussed above. The **r** *vs.* log T curves for these sets are almost superimposable with the corresponding pure primary effect curves. Again, the great similarity of the intramolecular effect and corresponding primary effect curves occurred regardless of the direction and temperature-dependence type of the individual corresponding secondary substitution effects.

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(29) Some of these sets were not part of our original collection[12] but were generated specifically for the present study.

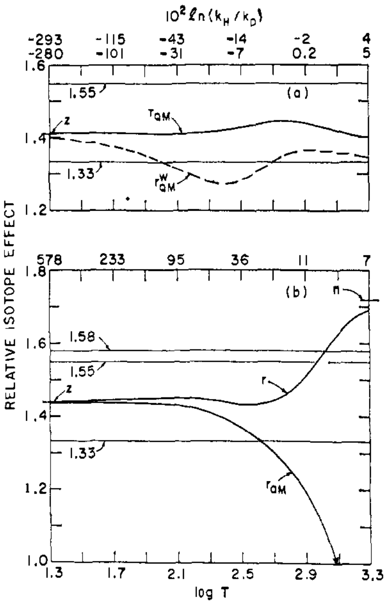

Figure 9. Relative tritium–deuterium isotope effects for individual low-magnitude-effect D and T cases exhibiting regular (types A and −A) temperature dependences. (a) and (b) correspond to curves (a) and (c), respectively, in Figure 10.

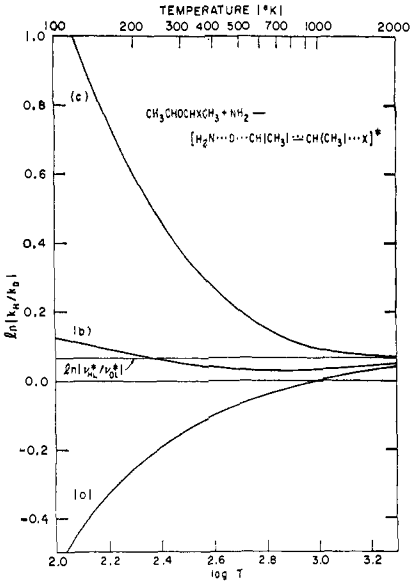

Figure 10. Low magnitude, pure primary, deuterium kinetic isotope effects: (a) original diag-ii force fields;[12] in the reactant f_{CH} = 4.5 mdyn/Å and in the transition state $f_{\mathrm{H\cdots NH}}$ = 0.47, $f_{\mathrm{H\cdots C\cdots C}} = f_{\mathrm{H\cdots CC}}$ = 0.34, $f_{\mathrm{H\cdots CH}}$ = 0.27, $f_{\mathrm{C\cdots H\cdots N}}$ = 0.1049 (mdyn Å)/rad²; (b) f_{CH} = 4.5 mdyn/Å, $f_{\mathrm{H\cdots NH}}$ = 0.34, $f_{\mathrm{H\cdots C\cdots C}} = f_{\mathrm{H\cdots CC}}$ = 0.27, $f_{\mathrm{H\cdots CH}}$ = 0.21, $f_{\mathrm{C\cdots H\cdots N}}$ = 0.075 (mdyn Å)/rad²; (c) f_{CH} = 5.0 mdyn/Å, $f_{\mathrm{H\cdots NH}} = f_{\mathrm{H\cdots C\cdots C}} = f_{\mathrm{H\cdots CC}}$ = 0.20, $f_{\mathrm{H\cdots CH}}$ = 0.15, $f_{\mathrm{C\cdots H\cdots N}}$ = 0.05 (mdyn Å)/rad². All other force constants as listed in ref 12.

Since most investigations of the role of quantum mechanical tunneling on isotopic rate constant ratios involve primary hydrogen isotope effects, it is worthwhile to consider such effects a little further. It appears that **r** for at least sizable magnitude, pure primary, *normal* ($k_1 > k_2$) effects, in the absence of tunneling greater than the Wigner term, should, at temperatures below ~1000°K, be restricted to the Bigeleisen range of 1.33–1.58. At low and intermediate temperatures it should be reasonably close to the Swain–Schaad approximation of 1.44. This conclusion is based not only upon our few results for pure primary effects but also for the type A secondary effects. The factor which led to a positive deviation from the 1.33–1.58 range for some of the type A secondary effects, *viz.*, small quantum effects $(R_{1/2}/N_{1/2})$ coupled with a high **n** value, is not a usual situation to obtain from an isotopic substitution at a primary position. The negative deviations from the 1.33–1.58 range observed for some of the type A secondary effects are not easily analyzed, but in any event are small. We can get some idea of the worst such behavior expected for primary isotope effects by examining the $\mathbf{r}_{\mathrm{QM}}$ *vs.* log *T* curves for the *inverse* (type −A) isotope effects observed with the same models of a β-elimination reaction that produced the negative deviation of **r** for the secondary effects. These five sets are probably the worst to be expected for primary effects because the reaction coordinates are very complicated and the low magnitude values of $|\ln (R_{1/2}/N_{1/2})|$ (0.22–0.29 at 300°K for D substitution) are not much larger than for a secondary isotope effect. Four of the five such type −A sets exhibited $\mathbf{r}_{\mathrm{QM}}$ *vs.* log *T* curves which appeared quite normal and resembled the ones shown for type +A effects in Figure 6. The fifth, which corresponded to a model with a very sharp barrier ($\nu_{\mathrm{1L}}{}^{\ddagger}$ = 1279*i* cm⁻¹) and had the smallest values of $|\ln (R_{1/2}/N_{1/2})|$ below ~850°K, was characterized by $\mathbf{r}_{\mathrm{QM}}$ and $\mathbf{r}_{\mathrm{QM}}{}^{\mathrm{W}}$ *vs.* log *T* curves somewhat different from the others. These are shown in Figure 9a. The Wigner-corrected curve does dip below 1.33, the minimum value of $\mathbf{r}_{\mathrm{QM}}{}^{\mathrm{W}}$ being ~1.27 at ~250°K. We must recognize, however, that even if this $\mathbf{r}_{\mathrm{QM}}{}^{\mathrm{W}}$ behavior were to appear with normal (type +A) effects, the **n** contribution would tend to raise **r** above the 1.33 line.

In order to test this conjecture we changed the force fields for this model by lowering slightly the primary hydrogen bending force constants in the transition state and raising slightly the CH stretching force constants in the reactant until the individual tritium and deuterium isotope effects became normal and regular. The temperature-dependence curves for the D-substitution reactions with the original[12] force field, the force field corresponding to the first normal regular case encountered, and one intermediate force field are shown in Figure 10. [It is interesting that the low magnitude pure primary D and T isotope effects corresponding to the intermediate force fields exhibited many types of temperature-dependence anomalies (inflections, extrema, and crossovers). This behavior will be discussed elsewhere.[28]] The relative isotope effect curves for the normal regular deuterium effect curve (c) in Figure 10 are shown in Figure 9b. It is apparent that $\mathbf{r}_{\mathrm{QM}}$ is headed toward a pole at high temperature. Thus, the type A curve in Figure 10 (curve c) is actually headed toward a crossover at some temperature above 2000°K. [In fact, because of the nature of the force constant changes in the model, the curve would have to exhibit two crossovers above 2000°K.[11] When the CH stretching force constants are raised still further in the reactant (to ~5.5 mdyn/Å), the high-temperature crossovers disappear.] Even with this atypical complicated model exhibiting a poorly behaved $\mathbf{r}_{\mathrm{QM}}$ curve, once the classical contribution **n** is included the complete r *vs.* log *T* curve becomes fairly well behaved, not

Table I. Range of Zero-Temperature (**z**) and Infinite-Temperature (**n**) Limits to Relative Tritium–Deuterium Isotope Effects

Isotopic substitution(s)	Type of force field[a]	Number of sets	**z**[b]	**n**[b]
Pure primary	diag-z	3	1.41, 1.41, 1.43	1.58, 1.91, 1.95
	diag-i	3	1.40, 1.41, 1.43	1.57, 1.71, 1.88
	diag-ii	5	1.40, 1.42, 1.44	1.57, 1.67, 1.72
	od	4	1.40, 1.42, 1.43	1.57, 1.79, 1.95
Pure secondary[c]	diag-z	26	0.37, 1.45, 1.51	1.84, 1.93, 1.98
	diag-i	14	−2.92, 1.41, 1.57	1.50, 1.73, 1.79
	diag-ii	14	−0.16, 1.41, 2.63	1.45, 1.61, 1.65
	od	16	−1.28, 1.46, 3.29	1.45, 1.69, 1.96
nfcc-like secondary	diag-z	17	1.44, 1.76, 1.93	1.87, 1.92, 1.98
	diag-i	5	1.48, 1.77, 1.89	1.40, 1.64, 1.82
	diag-ii	5	−0.08, 1.74, 1.78	1.36, 1.45, 1.48
	od	7	1.03, 1.72, 1.90	1.36, 1.71, 1.91
Simultaneous primary–secondary	diag-z	11	0.91, 1.40, 1.44	1.58, 1.85, 1.93
	diag-i	11	1.15, 1.40, 1.44	1.57, 1.71, 1.84
	diag-ii	11	1.34, 1.41, 1.99	1.57, 1.62, 1.71
	od	15	1.00, 1.38, 1.44	1.57, 1.80, 1.93
Intramolecular primary–secondary	diag-z	3	1.39, 1.42, 1.43	1.58, 1.89, 1.95
	diag-i	3	1.39, 1.42, 1.43	1.57, 1.71, 1.96
	diag-ii	3	1.37, 1.41, 1.42	1.57, 1.62, 1.73
	od	4	1.39, 1.41, 1.43	1.57, 1.82, 1.95

[a] diag-z represents a class of force fields with only diagonal force constants (F matrix elements) for reactants and transition states (except for those transition-state off-diagonal (interaction) force constants used to produce the reaction coordinates) and corresponding to flat potential barriers, diag-i represents a similar class of force fields corresponding to potential barriers of intermediate sharpness, diag-ii represents a similar class of force fields corresponding to very sharp potential barriers, and od represents a class of force fields including many off-diagonal force constants for both reactants and transition states (force fields corresponding to potential barriers ranging from flat to very sharp are grouped together in the od category). See ref 12 for a more detailed explanation and examples of the actual force fields used in the calculations. [b] The values are given in order as lowest, median, highest observed. [c] Isotopic substitution(s) at secondary atomic positions involved in significant force constant changes between reactant and transition state.

going outside the 1.33–1.58 range until ~1000°K. Examination of the Wigner-corrected curves for this set reveals that the corrections eliminate the high-temperature pole(s). The relative quantum effect $\mathbf{r}_{\mathrm{QM}}{}^{\mathrm{W}}$ exhibits a high-temperature negative deviation which is again overridden by the classical contribution.

We consider it dangerous to extend, without qualification, our conclusion about the expected good behavior of the relative isotope effects for sizable magnitude pure primary normal effects to mixed primary–secondary normal effects, despite the fact that such effects exhibiting type A temperature dependences produced well-behaved **r** *vs.* log T plots. The natures of the force constant changes at primary and secondary hydrogen positions can be quite different, so that simultaneous isotopic substitution at such positions might be prone to produce anomalous temperature behavior in the isotope effect.[12] As mentioned earlier, the relative isotope effects for anomalous cases can be quite irregular even when the temperature-dependence anomalies themselves are extremely difficult to detect experimentally. Figure 4e does, in fact, represent a case of mixed primary–secondary substitutions resulting in anomalous temperature behavior of the isotope effects (type E) and a corresponding irregular **r** *vs.* log T curve. In our study of the temperature dependences of kinetic isotope effects,[12] we found several cases of anomalous temperature behavior resulting from simultaneous substitutions at primary and secondary positions. Most of these isotope effects, however, were inverse ($k_1 < k_2$) throughout the 20–2000°K temperature region, and those that were normal over certain temperature intervals were characterized by low values of ln $R_{1/2}$. Probably, one can be confident in expecting relative tritium–deuterium isotope effects corresponding to mixed primary–secondary substitutions to be restricted to the 1.33–1.58 range below 1000°K, and near 1.44 at low and intermediate temperatures, if the individual isotope effects themselves (ln $R_{\mathrm{H/D}}$ and ln $R_{\mathrm{H/T}}$) are normal ($k_1 > k_2$) and large enough to be predominately manifestations of the primary substitutions.

At various points in the preceeding discussion, values of the zero-temperature limits **z** and the infinite-temperature limits **n** to the relative isotope effects were given. It is clear that the range of these limits is much larger than previously thought.[3,4] Table I lists, in categories, the ranges and approximate median values observed in this work. The various sets are grouped in the table without regard to the behavior of **r** at intermediate temperatures or to the temperature-dependence "type" of the individual isotope effects. In comparing **z**'s and **n**'s for specific related reaction sets, certain trends appeared, some of which are not necessarily reflected in the groupings of Table I. The value of **n** exhibited a definite trend to decrease as the potential barrier in the model was made sharper. A similar, but much less severe, trend in **z** was observed in many calculations, but sometimes **z** increased with increasing barrier sharpness. The value of **z** was usually significantly higher for an nfcc-like effect than for an effect in a similar calculation involving significant force constant changes at the isotopic position(s); no similar trend in **n** was observed. (However, most of our nfcc-like calculations for which such comparisons could be made involved only models with flat potential barriers.) Finally, there were usually no significant differences among either the values of **z** or the values of **n** for models in which the force fields were essentially diagonal (except for those off-diagonal force constants needed to produce a reaction coordinate[12]) and similar models in which many normal-magnitude off-diagonal force constants were included. Small differences did appear, however, when the transition-

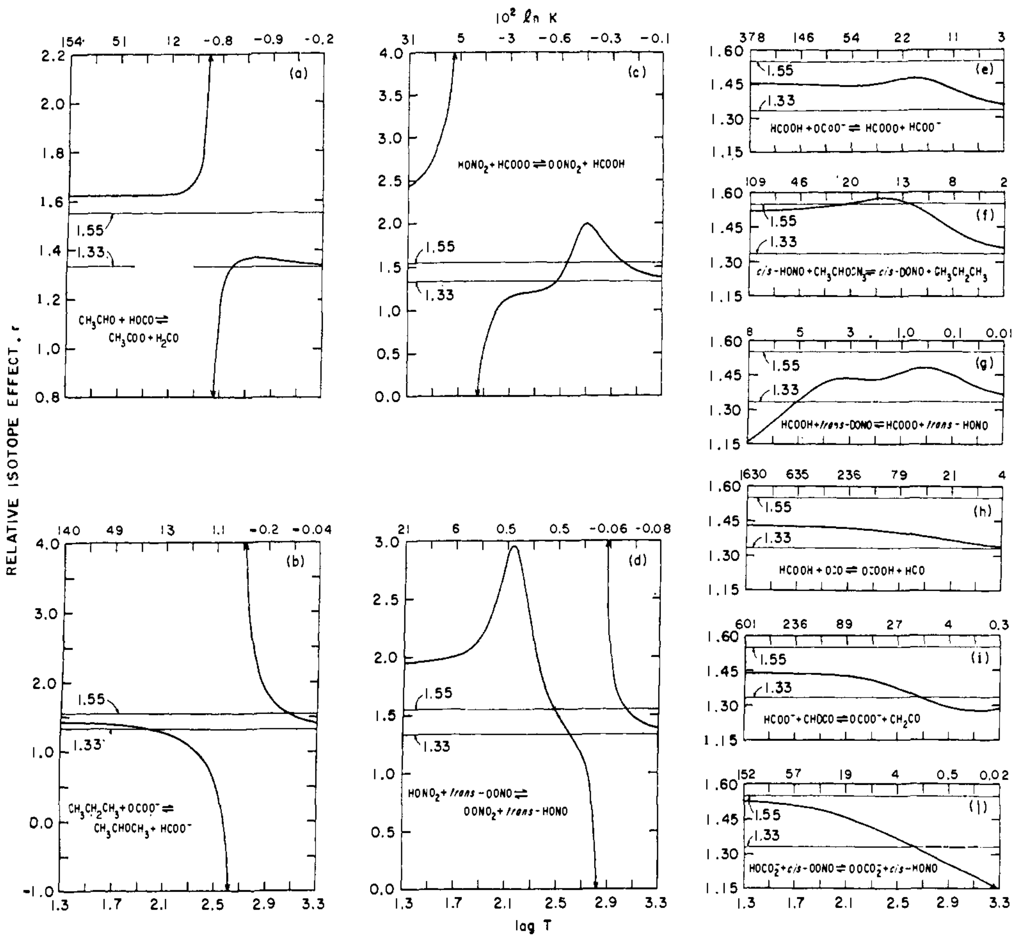

Figure 11. Typical relative tritium–deuterium equilibrium isotope effects. The individual isotope effects ($R_{H/D}$ and $R_{H/T}$) exhibit the following temperature-dependence types: (a) and (b) type D; (c) type I; (d) type H for deuterium substitution, type E for tritium substitution; (e), (f), and (g) type B; (h), (i), and (j) type A. Although the individual isotope effects for (j) exhibit nonanomalous temperature dependences throughout the 20–2000°K range, inversions at temperatures above 2000°K must occur because of the natures of the force fields. Thus, the curve in (j) appears headed toward a high-temperature pole. The input parameters for the equilibrium cases are given in ref 10 and 11.

state force fields contained off-diagonal force constants coupling reacting-bond motions to other valence coordinates, since the addition of such off-diagonal force constants tends to change the natures of the reaction coordinates somewhat.

Although our calculations showed differences in the **r** *vs.* log T behavior with reaction type, we do not feel that we can justifiably present correlations of relative tritium–deuterium isotope effects with reaction mechanisms. Our models were not designed to be the very best representations of specific reaction systems, but instead to encompass a large fraction of the types and magnitudes of force constant changes that might occur at hydrogen atoms in a large number of reaction types.

In order to assure ourselves that there was nothing special about rates, as compared to equilibria, or about the synthetic force fields we used for our kinetic isotope effect studies, we calculated corresponding tritium isotope effects for 66 of the 120 equilibrium deuterium isotope effects studied for their temperature dependences by Spindel, Stern, and Monse.[11,30] In these calculations spectroscopically derived force fields were used for the molecules. Since in every molecule the isotopic hydrogen atom is attached to another atom by a single bond, the equilibrium isotope effect systems are akin to our secondary kinetic isotope effect models. However, since the attaching atom was in some molecules carbon and in others oxygen, some of the equilibria considered are related to rather severe secondary effects. The **r** ($=\mathbf{r}_{QM}$) *vs.* log T curves for these equilibrium sets were very similar to the $\mathbf{r}_{QM}$ *vs.* log T curves for the kinetic isotope effect models, when considered in groupings according to the temperature dependences of the individual $R_{1/2}$ values. Specifically (i) when the $R_{1/2}$'s exhibit inversions (for equilibria inversions and crossovers are identical) the resulting **r** *vs.* log T plot exhibits a pole, with the value of **r** outside the 1.33–1.55 range as much as several hundred degrees in either direction from the inversion temperatures; (ii) sets with temperature-dependence anomalies of $R_{1/2}$ not associated with inversions can still have **r** values exhibiting large deviations from the 1.33–1.55 range, although not necessarily so (the degree of deviation generally increases with the "severity" of the anomaly); (iii) portions of some of the **r** *vs.* log T curves for anomalous $R_{1/2}$'s both with and without inversions looked like what might be predicted from earlier work[3-5] for large tunneling contributions (of course, tunneling can make no contribution to an equilib-

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(30) Spindel, *et al.*,[11] calculated temperature dependences of 120 equilibrium isotope effects involving monosubstitution with deuterium. In 54 of the cases, the reduced partition function ratio for substitution in a methyl group was taken as the geometric mean over the three methyl hydrogen positions. Since such a procedure introduces an approximation not inherent in eq 1, these cases were not considered in the present study.

rium isotope effect); (iv) regular (type A) isotope effects usually have **r** *vs.* log T curves confined to the 1.33–1.55 range and exhibiting relatively little structure [occasional exceptions were manifested in small negative deviations appearing in the high-temperature region ($T \approx 1000$°K) where, if exhibited by $\mathbf{r}_{QM}$ for *rates*, they would probably be washed out of **r** by **n**]; (v) in both anomalous and regular cases, the infinite-temperature asymptotic limit to **r** is 1.333, as demanded by theory[4] (this limit, however, can be approached from either above or below). Representative samples of the **r** *vs.* log T plots for the equilibrium isotope effect cases are shown in Figure 11.

It can be concluded from the work described in this report that one may use the usual estimates of **r** to calculate deuterium isotope effects from measured tritium effects, or *vice versa*, only if one is sure that the individual isotope effects are in the normal direction ($k_{\text{light}} > k_{\text{heavy}}$), reflect significant force constant changes at the isotopic position(s) between reactant and transition state, and exhibit regular (type A[10]) temperature behavior throughout the entire temperature range ($0 < T < \infty$). Present indications[2,12,28] are that one can only be so assured if one is dealing with sizable magnitude, pure primary, normal direction isotope effects and mixed primary–secondary normal isotope effects of sufficiently large magnitudes to be principally manifestations of the primary substitutions. Similarly, one should consider using relative tritium–deuterium isotope effects as indicators of quantum mechanical tunneling, or other factors not included in eq 1, only under the same conditions. Fortunately, these are the conditions most likely to be involved in a study of tunneling. We *estimate*, based on our studies, that if a primary or mixed primary–secondary deuterium isotope effect is at least as large as $\ln(k_H/k_D) = 1.0$ ($k_H/k_D \geqslant 2.7$) at 300°K, then the temperature-dependence behaviors of both the deuterium and corresponding tritium effects are most likely regular.

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A Study of Surface Structures of Submicron Metal Oxides by Vanadium Tetrachloride as a Paramagnetic Probe

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Abstract: The surface structures of annealed ($n = 1.4$OH/100 Å^2) and rehydrated ($n = 4.6$) Cabosils, γ-Al_2O_3, gibbsite, and boehmite have been studied by reactions with VCl_4. The vanadium atom becomes either singly or doubly attached depending upon whether the reaction consumes one or two hydroxyls as determined by HCl evolution. Reactions with annealed Cabosil have a stoichiometry of one. The incorporated vanadiums showed narrow epr lines at −195° which become significantly broadened at 25°. These species were readily reduced by heating the sample to above 150°. Therefore, nearly all of the paramagnetic probe molecules are singly attached and are within close approach to one another. Various alumina samples of different modifications react with VCl_4 to produce about 2HCl at 90°; the stoichiometry increases to 2.4 at higher temperatures. Therefore, all the vanadiums are doubly attached, and some of them even react with a third hydroxyl above 200°. The epr spectra of these species have line widths which are a function of degree of coverage alone but not of temperature. Heating to temperatures up to 450° caused no significant reductions. Reactions with rehydrated Cabosil consistently gave a stoichiometry of 1.5, suggesting that half of the vanadiums are singly attached and the remainder doubly attached. It is possible to deduce from the results of this study the approximate geometric distributions of hydroxyls on the surfaces of these submicron oxide particles.

The surfaces of solids, whether they are crystalline or amorphous, ionic or covalent, represent distinct states which differ chemically from the bulk states. The surface states may have unsaturated bonds (*i.e.*, the peripheral carbon atoms of a graphite crystal), or unsatisfied coordinations (*i.e.*, the Ti atoms along the c axis of the hexagonal α-$TiCl_3$), or polar functional groups. In the case of metal oxides, these groups are mostly hydroxyls. Ordinarily, the surface atoms only represent a minute fraction of the total. However, this fraction increases rapidly with the decrease of particle size. The surface hydroxyls (8OH/100 Å^2) of a typical sample of dried silica hydrogel with a surface area of 300 m^2 g^{-1}, amounts to 4% of the weight of the substance. Consequently, the surface groups largely determine the surface properties and usages of the substance. Submicron-sized oxides, which include fumed silica, alumina, TiO_2, mixed oxides, and also materials derived from them by appropriate chemical reactions, find diverse applications as adsorbents, reinforcing additives, processing aids, thixotropic agents, catalysts, and catalyst supports.

Many techniques have been employed in the past[1] to study the surface hydroxyls of metal oxides. These

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[1] H. P. Boehm, *Advan. Catal.*, 16, 179 (1966).