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Additivity of Contributions to Secondary Deuterium Kinetic Isotope Effects and Their Arrhenius Preexponential Factors. Toward a Method of Fitting Model Calculations to Experimental Data[1a]

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Abstract: The quantum secondary deuterium kinetic isotope effects due to individual force-constant changes, between reactant and transition state in a properly constructed model reaction, are, after accounting for a small easily determined correction factor, additive within the limits of usual experimental errors. A similar additivity relationship is found to be valid for the Arrhenius intercepts of the calculated isotope effects. These additivity relationships are used as the basis of a proposed systematic method of fitting model calculations to experimental data for purposes of reaction mechanism elucidation.

The effect of isotopic substitution on a reaction rate constant [kinetic isotope effect (kie)] can, in principle, be used to determine the force-constant changes that occur as the transition state is approached and thus can provide valuable information for the elucidation of the reaction mechanism. In recent years the fitting of digital computer model reactions to experimental data has come into fairly common use for this purpose. It has been pointed out[2] that a kinetic isotope effect measured at a single temperature might be interpreted as due to any of a number of force-constant changes or combinations of changes. Measurements of kie's due to several successive isotopic substitutions in the same reaction[3,4] and kie temperature dependences[2,4] have been suggested as possibilities for narrowing the range of possible interpretations.

The information available from kie temperature-dependence measurements can be separated into two types. The first concerns directly the variation in magnitude of the kie with varying temperature. It has been shown that, even within the harmonic approximation, secondary hydrogen kie's (as well as some other types of kie's) may be associated with temperature-dependence irregularities ("anomalies"), defined as deviations from smooth monotonic log–log plots of isotopic rate constant ratio (k_H/k_D) *vs.* temperature.[5] An observable temperature-dependence anomaly benefits model calculation force-field-fitting procedures by providing very exacting conditions for the force fields to satisfy. However, most secondary deuterium kie's are probably associated with regular (nonanomalous) temperature dependences. In addition, the anomalous region of a temperature-dependence curve might not fall within the range of experimental accessibility.

The second type of information obtainable from kie temperature-dependence measurements involves the preexponential factors of Arrhenius-type equations fitted to the experimental data. Generally, it is feasible to measure kie's experimentally only over small temperature ranges near room temperature. Over these small temperature ranges, an Arrhenius-type equation, given for rate constant ratios by

$$\ln (k_H/k_D) = \ln A + B/T \qquad (1)$$

has been found to fit the temperature dependences of experimental isotope effect results quite well. Wolfsberg and Stern[2] found that the Arrhenius preexponential factors A for model calculations of secondary deuterium isotope effects are dependent on the types of force-constant changes imposed in the models. They suggested[4] that a comparison of the A factors obtained from experimental secondary isotope effect data with the A factors obtained from model calculation data be used

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(2) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).

(3) A. Fry, *ibid.*, **8**, 409 (1964).

(4) M. J. Stern and M. Wolfsberg, *J. Pharm. Sci.*, **54**, 849 (1965).

(5) P. C. Vogel and M. J. Stern, *J. Chem. Phys.*, **54**, 779 (1971).

as one criterion of the fit of the models to the experimental results. Such comparisons have since been used for the above-stated purpose.[6]

Model calculation force-field fitting to experimental values of kie's and A factors has, heretofore, been carried out on a trial and error basis. In the present study we investigate the accuracy of certain additivity relationships for the secondary kie's and corresponding A factors associated with *individual* force-constant changes occurring in a reaction. A method incorporating these additivity relationships is proposed for constructing models to fit the observed kie values and A factors simultaneously. Such models should yield valuable information as to the specific force-constant changes, between reactant and transition state, involved in the reaction.

Preliminary Considerations

If an Arrhenius intercept (ln A) for a model calculation secondary deuterium isotope effect is approximately the sum of the intercepts associated with each force-constant change imposed separately, then one can use this additivity relationship to construct models all of which reproduce approximately the same (observed) A factor. If the same type of additivity relationship can be expected for the value of the kie [$\ln (k_H/k_D)$] at a particular temperature, then one can easily construct models that reproduce the experimentally observed kie. Combining the two additivity relationships should provide a method of choosing a model reaction force field that simultaneously reproduces the desired values of the kie and its corresponding Arrhenius preexponential factor. Such a data-fitting process would be less arbitrary and more orderly than constructing models by trial and error, and certainly less time consuming than fitting the two criteria iteratively. Even if this approach leads to a force field that only approximately fits the experimental data, at least it would provide a point at which to begin making small final adjustments.

We now consider just which quantities could possibly obey additivity relationships of the type discussed above. The complete kie at a particular temperature may be considered to be a sum of two terms[7]

$$\ln (k_H/k_D) = \ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}) + \ln (f \text{ ratio}) \qquad (2)$$

The first term is a purely classical, temperature-independent contribution reflective of the nature of the reaction coordinate; the second term is a purely quantum-mechanical, temperature-dependent contribution reflective of the isotopic shifts in the real vibrational frequencies of the reactant(s) and transition state. For secondary isotope effects the purely classical contribution $\ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$ is reasonably independent of the force-constant changes, between reactant and transition state, at the isotopic position(s), while the purely quantum-mechanical contribution ln (f ratio) is very force-field dependent, approaching zero in the absence of force-constant changes at the isotopic position(s).[2,8] Thus, each model calculation in which an individual force-constant change is imposed would produce a kie value (at a particular temperature) with a contribution from $\ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$, whereas a composite model in which several force-constant changes are imposed simultaneously would produce a kie value with only one such contributing term. Therefore, only ln (f ratio), not the complete kie, could possible be additive.

The Arrhenius preexponential factor A_f corresponding to the purely quantum-mechanical contribution, according to the equation

$$\ln (f \text{ ratio}) = \ln A_f + B/T \qquad (3)$$

is related to the A factor for the complete kie by

$$\ln A = \ln (\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}) + \ln A_f \qquad (4)$$

Thus, reasoning identical to that used above for the additivity of ln (f ratio) indicates that only ln A_f, not ln A, could possibly be additive.

One additional factor must be considered with respect to the additivity relationships under consideration. In order to determine the isotope effects and Arrhenius intercepts associated with individual force-constant changes, it is necessary to set up a "starting model" for a reaction in which, ideally, there are no force-constant or geometry changes, between reactant and transition state, at the isotopic position(s). However, since the geometry of the transition state is always taken as the final geometry desired (see Methods section), the starting model might indeed involve geometry changes at the isotopic position(s). Also, it may not be possible to eliminate all force-constant changes at the isotopic position(s). Both the geometry changes and force-constant changes will produce nonzero ln (f ratio) values for the starting model. Even when there is no force-constant or geometry change at the isotopic position(s), a model reaction will have a small but finite quantum kie [no force-constant change (nfcc) effect[8]]. This initial quantum kie, whatever its causes, is referred to in this report as the zeroth-order isotope effect [ln (f^0 ratio)]. Thus, the quantum kie produced by a given individual force-constant change in a calculation is composed of two parts: the isotope effect actually due to that given force-constant change, plus the zeroth-order isotope effect. As with the purely classical part of the kie, this zeroth-order term contributes only once in a composite model calculation. Consequently, ln (f^0 ratio) must be subtracted from the ln (f ratio) values produced by individual force-constant changes and from the composite model ln (f ratio) value before comparison can be made. The zeroth-order isotope effect has an associated Arrhenius intercept, the zeroth-order intercept ln A_f^0, for which account must also be taken. The additivity relationships to be tested are then

$$\ln (f \text{ ratio})_{\text{composite}} = \sum_i^n \ln (f \text{ ratio})_i - (n - 1) \ln (f^0 \text{ ratio}) \qquad (5)$$

and

$$\ln A_{f,\text{composite}} = \sum_i^n \ln A_{f,i} - (n - 1) \ln A_f^0 \qquad (6)$$

where the sum index i is taken over the different kinds[9] of nonzero force-constant changes considered.

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[6] See, for example, A. V. Willi, *J. Amer. Chem. Soc.*, **90**, 5999 (1968).

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

[8] M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 2618 (1966).

[9] The designation "kind" is used to distinguish the force constants associated with one particular set of equivalent, or very nearly equivalent, internal coordinates from those associated with another set (*e.g.*, CH stretching from CX stretching, HCC bending from HCX bending, CH stretching from HCH bending, etc.). Force constants of a given kind are assigned identical values.

Methods

All kie calculations are carried out within the framework of the statistical-thermodynamic, transition-state theory treatment of such effects in the harmonic approximation.[7] In setting up a starting model for a reaction, a reactant is chosen with geometry and force field considered reasonable for the system under consideration. Since kie's reflect essentially force-constant *changes* between reactant and transition state,[2,7] the detailed choice of reactant geometry and force field is not critical. The transition-state geometry is chosen as the final geometry desired, some reasonable configuration intermediate between reactant(s) and product(s). It has been shown[2] that the effects on kie's of geometry changes, between reactant and transition state at the isotopic position(s), are usually small and, in any event, inseparable from the effects of actual force-constant changes. The starting transition-state force constants are chosen as close to their corresponding reactant values as possible.

Because kie's reflect essentially *local* force-constant changes at the isotopic position(s),[8,10] it is only necessary to consider variations in transition-state force constants for those internal coordinates that involve the isotopic position(s) directly. In this study the force-constant changes of interest are those for the stretching and all of the bond-angle-bending internal coordinates involving the isotopic position(s). Each kind of transition-state force constant of interest is varied separately, in stages, and the resulting kie's are calculated, at 50 temperatures over the temperature range 20–2000°K, using computer programs described previously.[11,12] Each corresponding A_t factor is determined by least-squares fitting[13] of four unweighted ln (f ratio) values over the temperature range 300–375°K.

Plots of ln (f ratio)$_i$ at 300°K and $A_{t,i}$ as functions of the values of individual kinds of transition-state force constants are prepared. A desired value of ln (f ratio) at 300°K for the composite model is chosen to approximate the values found experimentally for the type of isotopic substitution and reaction being considered. By interpolating from the above-mentioned plots of ln (f ratio)$_i$ *vs.* transition-state force constant, individual force-constant changes are combined in such a manner as to fit Σ_i ln (f ratio)$_i$ to the desired value of the composite ln (f ratio), as would be done if one were working with actual experimental data. The A_t factors corresponding to the chosen individual force-constant changes are also determined by graphical interpolation. Finally, the individual force-constant changes are combined into a composite model whose actual quantum kie and preexponential factor are calculated and used to test the additivity relationships expressed by eq 5 and 6. The procedure is repeated with several different sets of force-constant changes, all "fitted" to approximately the same composite ln (f ratio) value.

For each calculation, whether involving an individual force-constant change or a composite of such, the kie over the entire 20–2000°K range is plotted and examined for the presence of a temperature-dependence anomaly,[5] since the existence of such an anomaly could invalidate the extrapolation process used to determine the Arrhenius intercept and thus make any conclusion based on the value of the intercept subject to question. Unless specifically indicated otherwise, the temperature dependence of each model calculation kie discussed in this report is regular (nonanomalous). In actual experimental practice undetected temperature-dependence anomalies might present problems. One should be particularly suspicious of the presence of a temperature-dependence anomaly when the magnitude of an observed kie is low.[5] In the present investigation cases with temperature-dependence anomalies generally did not exhibit additivity properties significantly different from similar cases with regular temperature dependences (see Results section).

One additional item should be mentioned. Experimentally, one measures the complete kie, not just the quantum-mechanical contribution. Although no reliable method has yet been developed to separate the purely classical and purely quantum-mechanical parts of a kie determined experimentally around the room-temperature region, a very simple model calculation, such as that used to determine the zeroth-order corrections, can provide a reasonable estimate of the (temperature-independent) classical part. Since for secondary isotope effects the purely classical contribution is nearly independent of the force constants of interest [except in unusual cases where a bond-angle-bending coordinate(s) involving the isotopic position(s) is an integral part of the reaction coordinate], using the quantum kie and A_t as criteria of model calculation fitting is almost equivalent to using the complete kie and A.

Model Systems

Because kie's reflect essentially local force-constant changes at the isotopic position(s),[8,10] using only a limited number of models it is possible to study a large fraction of the types and magnitudes of force-constant changes assumed to be operative in any reaction. Eight cases of isotopic substitutions and overall kie magnitudes in four general model types were chosen to represent the reaction types decarboxylation, elimination, and nucleophilic substitution. The general model types are: (i) unimolecular substitution (SN1) of ethyl-X (X is an "atom" with atomic mass 80, representative of halogen or any heavy group[10]); (ii) bimolecular β-hydrogen elimination (E2) from modified alkyl-X with amide ion; (iii) decarboxylation of modified malonic acid; (iv) bimolecular substitution (SN2) of ethyl-X with another X atom. These reactions are depicted in Figure 1. The β-elimination and decarboxylation models employ the "cutoff" procedure,[10] in which atoms removed from the site(s) of isotopic substitution may be eliminated. A complete list of the input parameters (geometries and force fields) for the starting models is available.[14] The cases considered include examples of

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

[11] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

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

[13] M. E. Schneider, Ph.D. Thesis, Yeshiva University, New York, N. Y., 1971.

[14] Listings of the input parameters for the starting models will appear immediately following these pages in the microfilm edition of this volume of the journal. Appearing also will be force-field data, in the form of Table I, for all of the other cases considered in this work. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1355. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

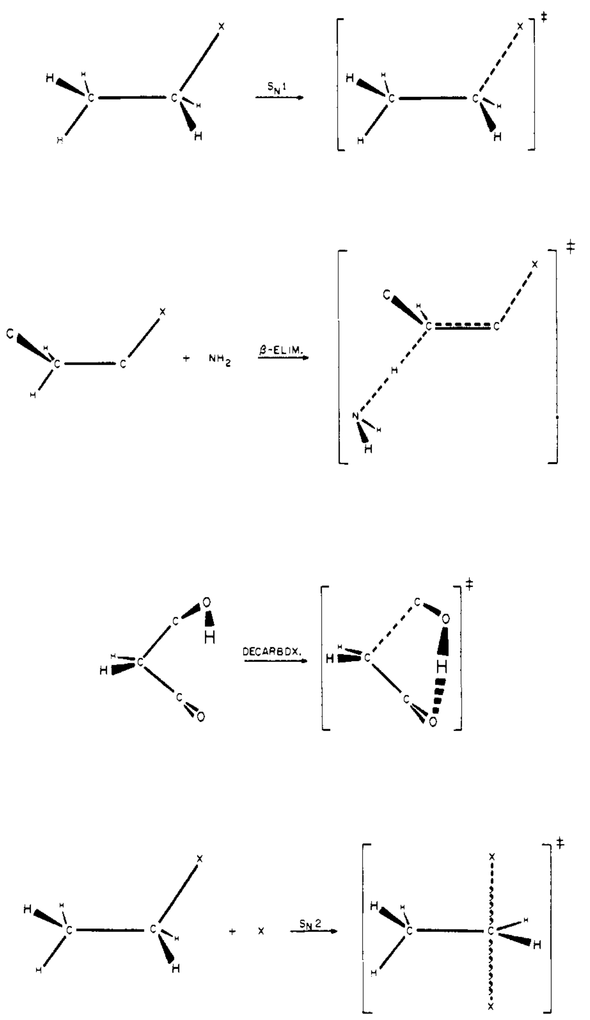

Figure 1. Model reaction types.

normal and inverse kie's, α-secondary and β-secondary kie's, single, double, and triple deuterium substitutions, and simple and complex reaction coordinates.

Two cases of isotopic substitution are considered in the SN1 model: α-D_2 and β-D_3. The geometries of the reactant and transition state are identical and the starting force constants differ only in that in the transition state the C$\cdots$X stretching force constant is set equal to zero. Thus, the reaction coordinate corresponds to simple CX bond rupture on a limiting flat potential barrier (reaction coordinate frequency $\nu_L^{\ddagger}$ equals zero). The zeroth-order kie's for these cases are true nfcc effects,[8] so that the zeroth-order correction terms, ln (f^0 ratio) and ln A_1^0, should be very small. For the α-D_2 substitution individual kinds of stretching and bending force-constant changes were combined in 11 different ways, such that for each combination the expected composite ln (f ratio) was ~0.30 at 300°K. For the β-D_3 substitution individual kinds of force-constant changes were combined in 15 different ways, such that for each combination the expected composite ln (f ratio) was ~0.23 at 300°K. Because of the presence of the X atom on the primary ethyl carbon, there is no way of choosing a static geometry for this model that will result in the three β-hydrogen atoms being exactly equivalent. In reality, they are equivalent because of internal rotation about the CC bond. The false unequivalency is, for the purposes of this study, unimportant; the three β-hydrogen atoms are treated in this work as equivalent for purposes of grouping force constants into "kinds."[9]

The β-elimination model is a cutoff version[10,15] of a model for the reaction between *sec*-butyl-X and amide ion.[5] The cutoff reactants are amide ion and modified alkyl-X. Isotopic substitution is made at the secondary hydrogen position (*i.e.*, the one *not* directly involved in the bond-making–bond-breaking process) on the methylene carbon (α-D_1 substitution). The transition state is chosen to reflect about half passage to the products, ammonia, modified alkene, and X^-. The reaction coordinate corresponds to concerted transformation of four bonds: loosening of the C$\cdots$H and C$\cdots$X bonds, and tightening of the C$\overset{\cdots}{-}$C and N$\cdots$H bonds. The reaction coordinate frequency $\nu_L^{\ddagger}$ is imaginary and of intermediate magnitude, corresponding to an intermediately curved potential barrier. The zeroth-order isotope effect consists of contributions from both nfcc effects and geometry-change effects. Individual stretching and bending force-constant changes were combined in 19 different ways, such that for each combination the expected composite ln (f ratio) was ~0.15 at 300°K.

The decarboxylation model is a cutoff version[10,15] of a model for the decarboxylation of malonic acid.[5] Isotopic substitution is made at the two methylene hydrogens (α-D_2 substitution) which are treated as equivalent for purposes of grouping force constants into "kinds."[9] The transition state is chosen as leading to modified (cutoff) CO_2 and the enol form of modified acetic acid. The reaction coordinate corresponds to the simultaneous rupture of a CC bond and formation of an OH bond in the cyclic transition state. The potential energy barrier has intermediate curvature. The zeroth-order isotope effect is due to both nfcc effects and geometry-change effects. Individual stretching and bending force-constant changes were combined in 20 different ways, such that for each combination the expected composite ln (f ratio) was ~0.30 at 300°K.

The isotopic substitution considered in the SN2 model is α-D_2. The transition state has a trigonal-bipyramidal structure about the reaction center, with bond lengths adjusted to reflect sp^2-like hybridization at the primary carbon atom. The reaction coordinate corresponds to antisymmetric X$\cdots$C$\cdots$X stretching. The potential energy barrier has intermediate curvature. The zeroth-order isotope effect for this model type presents a problem not encountered with the other model types. In the transition state each α-hydrogen atom is involved in two HC$\cdots$X bending coordinates, while in the reactant each α-hydrogen atom is involved in only one HCX bending coordinate with force constant 0.53 mdyn Å/rad^2. In order to keep the zeroth-order isotope effect ln (f^0 ratio) as small as possible, in the zeroth-order transition-state force field the force constants for all four of the HC$\cdots$X bending coordinates are taken as 0.53/2 mdyn Å/rad^2. Thus, the force-constant increase for two of the coordinates (0 →

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[15] In the "cutoff" models, more atoms were retained than the minimum permitted[10] in order to maintain the nature of the reaction coordinate and/or to allow the same model to be used for purposes outside of the present investigation.[13]

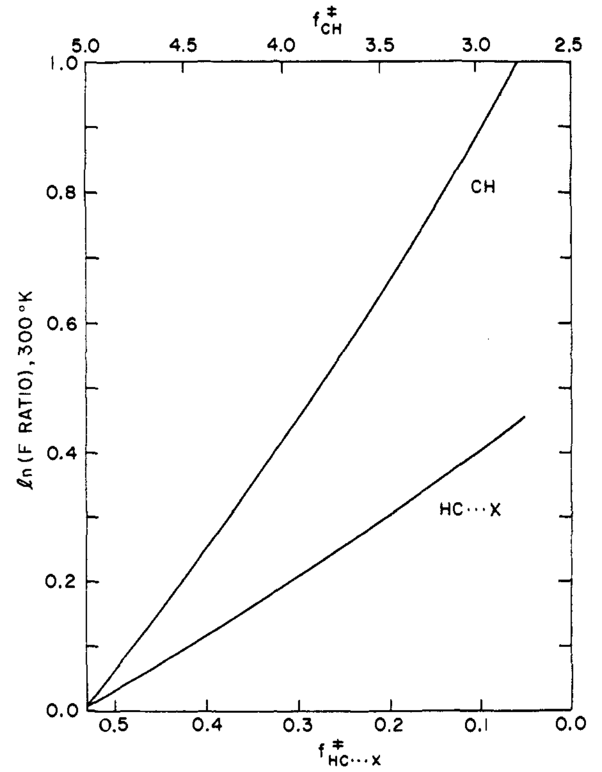

Figure 2. Quantum kinetic isotope effect as function of individually varied transition-state force constants in α-D$_2$ SN1 models.

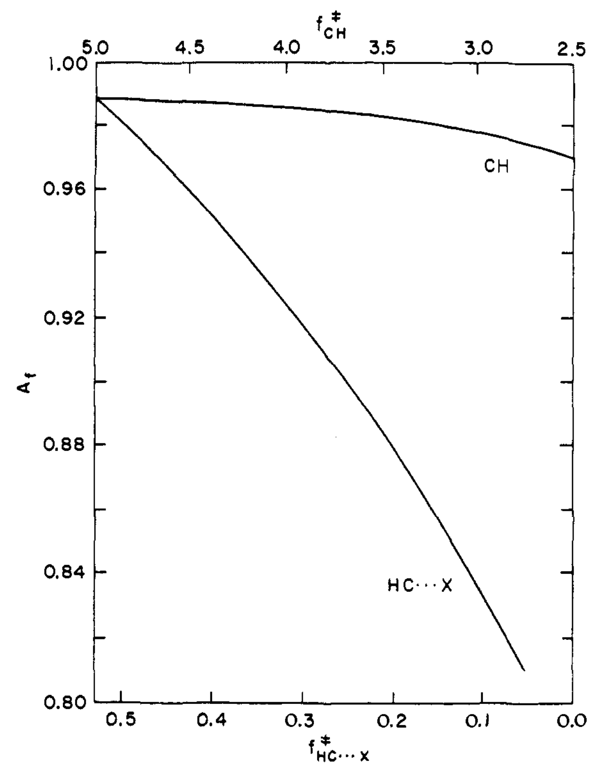

Figure 3. Arrhenius preexponential factor as function of individually varied transition-state force constants in α-D$_2$ SN1 models.

0.53/2) is compensated by the decrease for the other two coordinates (0.53 → 0.53/2). This zeroth-order force field is designated "C" (for compensatory). The "C" ln (f^0 ratio) does, of course, contain contributions from geometry changes.

A second method of choosing a zeroth-order transition-state force field is used specifically to investigate the effect of a large ln (f^0 ratio) correction term on the additivity relationships. Here the force constants for all four HC···X bending coordinates are set at 0.53 mdyn Å/rad^2, *i.e.*, at the value of the two HCX bending force constants in the reactant. This zeroth-order force field is designated "N" (for noncompensatory). The "N" ln (f^0 ratio) has contributions from both geometry changes and force-constant changes (0 → 0.53 for two of the HC···X bending coordinates) at the isotopic positions. For the SN2 models individual force-constant changes were combined in several different ways (20 for the "C" models; 20 for the "N" models) such that for each combination the expected composite ln (f ratio) was ~0.14 at 300°K, and in several different ways in addition (20 for the "C" models; 19 for the "N" models) such that the expected composite ln (f ratio) was *ca.* −0.12 at 300°K. The latter cases correspond to inverse isotope effects.

Results

The ln (f ratio) values for the composite models were obtained as "exact" quantities. They are presented to four decimal places in the following tables. In presenting individual ln (f ratio)$_i$ values and values derived from such, the fourth decimal places are set with inferior numerals to indicate that the graphical interpolation procedure was estimated to involve uncertainties of more than about three units in that place. Seldom, if ever, can a secondary deuterium kie be measured to more than three decimal places. The additional place is retained here for more precise error analysis.

The estimated standard deviations of the ln A_f values obtained using "exact" ln (f ratio) values were typically on the order of 0.0001–0.001 (somewhat higher, on the order of 0.002 and as high as 0.003, for the SN2, ln (f ratio) ≈ 0.14, "N" models). Such, then, represents the *minimum* error associated with ln A_f values derived from actual experimental data. Four decimal places are retained in the error analysis. The graphical interpolation procedure used to determine the individual ln $A_{f,i}$ values was estimated to introduce uncertainties of less than two or three units in the fourth decimal place of any of the associated values presented in the tables.

α-D$_2$ Substitution in SN1 Model Reaction. Figure 2 shows plots of quantum kie at 300°K as a function of individually varied transition-state force constants for the CH stretching coordinates and one kind of bending coordinates. Figure 3 shows the corresponding A_f *vs.* force-constant plots. Table I lists the particular transition-state force constants used in each of the composite calculations.[14] Tables II and III are detailed listings of the results of the additivity relationships evaluation.[16] It is seen from Table III that the additivity relationships, as expressed by eq 5 and 6, are obeyed accurately, the errors being no larger in magnitude than those associated with experimental data.

β-D$_3$ Substitution in SN1 Model Reaction. Results of

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(16) With regard to the recipe given in the Methods section, for each composite model the individual isotope effects and Arrhenius intercepts in Table II, corresponding to the individual force-constant changes in Table I, were determined by graphical interpolation of Figures 2 and 3 (and similar figures for f_{HCC} and f_{HCH}) and used to determine the Σ_i values of Table III, according to the formulas given in footnote *b* of Table III.

Table I. Transition-State Force Constants Varied in α-D_2 SN1 Composite Models[a]

Composite[b]	f_{CH}	$f_{HC\cdots X}$	f_{HCC}	f_{HCH}
z-o[c]	5.0	0.53	0.68	0.53
A	4.514	0.420	0.68	0.53
B	4.639	0.53	0.5005	0.53
D	4.639	0.420	0.68	0.4665
E	4.889	0.53	0.623	0.2655
F	4.763	0.420	0.623	0.4665
G	4.639	0.478	0.623	0.4665
H	4.889	0.443	0.561	0.4375
J	5.0	0.420	0.561	0.3955
K	5.0	0.478	0.5005	0.3955
L	5.0	0.420	0.4415	0.53
M	5.0	0.363	0.68	0.329

[a] The force constants apply to all internal coordinates satisfying the subscript designation and involving an isotopic position(s). The units of the stretching force constants (f_{CH}) are mdyn/Å. The units of the bending force constants ($f_{HC\cdots X}$, f_{HCC}, f_{HCH}) are mdyn Å/rad^2. [b] The composite model letter designations in this and in the following tables are arbitrarily assigned for purposes of identification. There is no correspondence between the letter designations for different cases. Thus, for example, composite model B for the α-D_2 SN1 case (Tables I–III) bears no relationship to composite model B for any of the other cases (Tables IV–X). [c] Zeroth-order model.

Table II. Individual Contributions to Quantum Kie's and Arrhenius Intercepts for α-D_2 SN1 Models

	10^4 ln (f ratio)$_i$, 300°K[a,b]				10^4 ln $A_{f,i}$[a,c]			
Composite	CH	HC···X	HCC	HCH	CH	HC···X	HCC	HCH
A	200_0	100_0			−129.8	−435		
B	150_0		150_0		−125.8		−537	
D	150_0	100_0		50_0	−125.8	−435		−193
E	50_0		50_0	200_0	−120.7		−240	−547
F	100_0	100_0	50_0	50_0	−123.8	−435	−240	−193
G	150_0	50_0	50_0	50_0	−125.8	−260	−240	−193
H	50_0	80_0	100_0	70_0	−120.7	−364	−380	−230
J		100_0	100_0	100_0		−435	−380	−295
K		50_0	150_0	100_0		−260	−537	−295
L		100_0	200_0			−435	−706	
M		150_0		150_0		−626		−410

[a] Determined by graphical interpolation; uncorrected for zeroth-order effects. [b] Estimated precision of interpolation better than ~±0.0006. [c] Estimated precision of interpolation better than ~2 units in last place given.

Table III. Additivity Relationships Evaluation for α-D_2 SN1 Models

		10^4 ln (f ratio), 300°K			10^4 ln A_f			10^4 ln
Composite	Composition code[a]	Σ_i[b]	Composite	Error[c]	Σ_i[b]	Composite	Error[c]	$(\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$[e]
z-o[d]			69			−118		338
A	s1b	293_1	2935	0_4	−447	−447	0	338
B	s1b	293_1	2929	-0_2	−545	−544	1	338
D	s2b	286_2	2862	0_0	−518	−522	−4	338
E	s2b	286_2	2887	2_5	−671	−673	−2	338
F	s3b	279_4	2812	1_8	−638	−642	−4	338
G	s3b	279_4	2808	1_4	−465	−466	−1	338
H	s3b	279_4	2819	2_5	−740	−756	−16	338
J	3b	286_2	2896	3_4	−875	−896	−21	338
K	3b	286_2	2892	3_0	−857	−874	−17	338
L	2b	293_1	2951	2_0	−1024	−1044	−20	338
M	2b	293_1	2960	2_9	−918	−942	−24	338

[a] The composition code indicates the number of different *kinds* of transition-state force constants that are varied from the zeroth-order model. In the s*n*b designation: the presence of s indicates one kind of stretching force constant, f_{CH}, is varied; b indicates that bending force constants are varied; n is number of different kinds of bending force constants varied. [b] Σ_i refers to $\Sigma_i^n \ln (f \text{ ratio})_i - (n-1) \ln (f^0 \text{ ratio})$ or $\Sigma_i^n \ln A_{f,i} - (n-1) \ln A_f^0$. See text for discussion of precision. [c] Error = composite − Σ_i. [d] Zeroth-order model. [e] The transition-state force fields for these models were chosen in such a manner as to make the reaction coordinate frequency $\nu_L^{\ddagger}$, corresponding to C···X stretching, exactly zero. Thus, the reaction coordinate separates out as a normal mode and $\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$ is completely independent of force constants involving the isotopic positions.

the additivity relationships evaluation are given in Table IV. The composite values of ln (f ratio) and ln A_f are again in excellent agreement with the corresponding sums of individual values; the errors are again in the range of, or smaller than, expected experimental errors.

α-D_1 Substitution in β-Elimination Model Reaction. In this case the zeroth-order quantum isotope effect ln (f^0 ratio) is inverse and of low magnitude, but possessive of a regular temperature dependence. Because of this low magnitude each of the individual force-constant changes (decreases between reactant and transition state) applied resulted in normal direction quantum kie's [ln (f ratio) > 0]. Very small force-constant changes resulted in ln (f ratio)'s that exhibited minor temperature-dependence anomalies in the form of inflection regions. No force-constant change to be combined in a composite model was taken from these regions of anomalous temperature dependences and none of the composite models produced temperature-dependence abnormalities. Numerical results are given in Table V. Again, the additivity relationships are obeyed accurately.

α-D_2 Substitution in Decarboxylation Model Reaction. The zeroth-order isotope effect exhibits a crossover (a change in the direction of the kie with respect to the classical, infinite-temperature limit) in the room-temperature region (crossover temperature ~325°K). None of the kie's produced by the individual force-constant changes studied are characterized by temperature-dependence anomalies, nor are any of the kie's of the composite-molecule models.

Results of the additivity relationships evaluation are

Table IV. Additivity Relationships Evaluation for β-D_3 SN1 Models

Composite	Composition code[a]	$10^4 \ln$ (f ratio), 300°K			$10^4 \ln A_f$			$10^4 \ln$ $(\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$[e]
		Σ_i^b	Composite	Error[c]	Σ_i^b	Composite	Error[c]	
z-o[d]			8			−17		262
A	s1b	229$_2$	2299	0$_7$	−111	−111	0	262
B	s1b	229$_2$	2302	1$_0$	−166	−166	0	262
C	s1b	229$_2$	2293	0$_1$	−354	−354	0	262
D	s1b	229$_2$	2300	0$_8$	−359	−359	0	262
E	s1b	229$_2$	2308	1$_6$	−534	−534	0	262
F	s2b	228$_4$	2290	0$_6$	−159	−159	0	262
G	s2b	228$_4$	2296	1$_2$	−431	−434	−3	262
H	s2b	228$_4$	2304	2$_0$	−487	−492	−5	262
I	s2b	228$_4$	2297	1$_3$	−388	−391	−3	262
J	s2b	228$_4$	2308	2$_4$	−484	−489	−5	262
K	2b	229$_2$	2306	1$_4$	−680	−682	−2	262
L	2b	229$_2$	2299	0$_7$	−484	−485	−1	262
M	2b	229$_2$	2306	1$_4$	−557	−562	−5	262
N	2b	229$_2$	2297	0$_5$	−526	−532	−6	262
O	2b	229$_2$	2318	2$_6$	−619	−624	−5	262

[a–e] See corresponding footnotes to Table III.

Table V. Additivity Relationships Evaluation for α-D_1 β-Elimination Models

Composite	Composition code[a]	$10^4 \ln$ (f ratio), 300°K			$10^4 \ln A_f$			$10^4 \ln$ $(\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$
		Σ_i^b	Composite	Error[c]	Σ_i^b	Composite	Error[c]	
z-o[d]			−49			13		84
A	s1b	154$_9$	1546	−0$_3$	−159	−159	0	84
B	s1b	154$_9$	1544	−0$_5$	−254	−253	1	75
C	s1b	154$_9$	1554	0$_5$	−125	−126	−1	81
D	s1b	154$_9$	1550	0$_1$	−147	−147	0	79
E	s2b	159$_8$	1610	1$_2$	−257	−271	−14	79
F	s2b	159$_8$	1592	−0$_6$	−217	−221	−4	78
G	s2b	159$_8$	1599	0$_1$	−306	−313	−7	80
H	s2b	159$_8$	1593	−0$_5$	−279	−282	−3	80
I	s3b	164$_7$	1653	0$_6$	−294	−307	−13	78
J	s3b	164$_7$	1653	0$_6$	−309	−323	−14	78
K	s3b	164$_7$	1654	0$_7$	−306	−320	−14	77
L	3b	159$_8$	1630	3$_2$	−379	−402	−23	76
M	3b	159$_8$	1623	2$_5$	−375	−397	−22	78
N	3b	159$_8$	1619	2$_1$	−398	−415	−17	75
O	3b	159$_8$	1631	3$_3$	−384	−405	−21	75
P	2b	154$_9$	1585	3$_6$	−352	−379	−27	78
Q	2b	154$_9$	1553	0$_4$	−447	−454	−7	76
R	2b	154$_9$	1561	1$_2$	−432	−439	−7	71
S	2b	154$_9$	1558	0$_9$	−407	−414	−7	70

[a–d] See corresponding footnotes to Table III.

Table VI. Additivity Relationships Evaluation for α-D_2 Decarboxylation Models

Composite	Composition code[a]	$10^4 \ln$ (f ratio), 300°K			$10^4 \ln A_f$			$10^4 \ln$ $(\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger})$
		Σ_i^b	Composite	Error[c]	Σ_i^b	Composite	Error[c]	
z-o[d]			5			−43		184
A	s1b	299$_5$	2992	−0$_3$	−461	−463	−2	178
B	s1b	299$_5$	3003	0$_8$	−445	−444	1	178
C	s1b	299$_5$	3005	1$_0$	−794	−793	1	174
D	s1b	299$_5$	3000	0$_5$	−191	−192	−1	182
E	s2b	299$_0$	3009	1$_9$	−479	−488	−9	177
F	s2b	299$_0$	2994	0$_4$	−310	−313	−3	180
G	s2b	299$_0$	3010	2$_0$	−578	−591	−13	176
H	s2b	299$_0$	3011	2$_1$	−663	−677	−14	175
I	s3b	298$_6$	3016	3$_0$	−543	−557	−14	176
J	s3b	298$_6$	3012	2$_6$	−514	−523	−9	177
K	s3b	298$_6$	3014	2$_8$	−600	−614	−14	175
L	s3b	298$_6$	3025	3$_9$	−673	−692	−19	174
M	3b	299$_0$	3023	3$_3$	−816	−835	−19	172
N	3b	299$_0$	3021	3$_1$	−687	−708	−21	174
O	3b	299$_0$	3022	3$_2$	−717	−739	−22	174
P	3b	299$_0$	3027	3$_7$	−731	−757	−26	173
Q	2b	299$_5$	3018	2$_3$	−781	−798	−17	173
R	2b	299$_5$	3010	1$_5$	−705	−715	−10	175
S	2b	299$_5$	3014	1$_9$	−882	−899	−17	171
T	2b	299$_5$	3017	2$_2$	−723	−745	−22	173

[a–d] See corresponding footnotes to Table III.

Table VII. Additivity Relationships Evaluation for α-D_2 SN2 "N" Models [ln (f ratio) ≈ −0.12]

Composite	Composition code[a]	10^4 ln (f ratio), 300°K			10^4 ln A_t			10^4 ln
		Σ_i[b]	Composite	Error[c]	Σ_i[b]	Composite	Error[c]	($\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$)
z-o[d]			−4424			1301		411
C	s1b	-119_6	−1193	0_3	533	533	0	355
G	s2b	-119_2	−1184	0_8	656	659	3	373
H	s2b	-119_2	−1204	-1_2	680	685	5	402
I	s3b	-118_8	−1175	1_3	647	646	−1	372
J	s3b	-118_8	−1167	2_1	804	790	−14	397
L	3b	-119_2	−1148	4_4	641	611	−30	393
M	3b	-119_2	−1144	4_8	710	681	−29	404
N	3b	-119_2	−1136	5_6	582	546	−36	402
O	3b	-119_2	−1188	0_4	507	507	0	381
P	2b	-119_6	−1119	7_7	709	653	−56	411
Q	2b	-119_6	−1193	0_3	687	689	2	388
R	2b	-119_6	−1122	7_4	535	480	−55	411
S	2b	-119_6	−1198	-0_2	484	489	5	382
Models Producing High-Temperature Crossovers[e]								
A	s1b	-119_6	−1219	-2_3	823	825	2	411
B	s1b	-119_6	−1215	-1_9	1223	1224	1	411
D	s1b	-119_6	−1200	-0_4	1088	1090	2	397
E	s2b	-119_2	−1185	0_7	783	785	2	392
F	s2b	-119_2	−1192	0_0	1086	1134	48	411
K	s3b	-118_8	−1191	-0_3	923	922	−1	404

[a–d] See corresponding footnotes to Table III. [e] Crossover temperatures in 650–1500°K range.

Table VIII. Additivity Relationships Evaluation for α-D_2 SN2 "N" Models [ln (f ratio) ≈ 0.14]

Composite	Composition code[a]	10^4 ln (f ratio), 300°K			10^4 ln A_t			10^4 ln
		Σ_i[b]	Composite	Error[c]	Σ_i[b]	Composite	Error[c]	($\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$)
z-o[d]			−4424			1301		411
A	s1b	142_4	1419	-0_5	−723	−722	1	411
B	s1b	142_4	1413	-1_1	507	506	−1	411
C	s1b	142_4	1416	-0_8	−77	−74	3	309
D	s1b	142_4	1424	0_0	564	565	1	360
E	s2b	140_8	1535	12_7	515	415	−100	411
F	s2b	140_8	1416	0_8	−252	−247	5	323
G	s2b	140_8	1414	0_6	232	232	0	364
H	s2b	140_8	1395	-1_3	83	83	0	395
I	s3b	141_2	1572	16_0	96	−6	−102	378
J	s3b	141_2	1427	1_5	436	428	−8	364
K	s3b	141_2	1532	12_0	318	230	−88	395
L	s3b	141_2	1642	23_0	291	110	−181	405
M	3b	140_8	1629	22_1	38	−128	−166	386
N	3b	140_8	1429	2_1	−362	−378	−16	374
O	3b	140_8	1468	6_0	−12	−48	−36	355
P	3b	140_8	1553	14_5	−75	−182	−107	374
Q	2b	142_4	1467	4_3	−861	−898	−37	411
R	2b	142_4	1215	-20_9	−283	−281	2	357
S	2b	142_4	1422	-0_2	−18	−17	1	364
T	2b	142_4	1431	0_7	−375	−370	5	324

[a–d] See corresponding footnotes to Table III.

presented in Table VI. In this case, the ln (f ratio) additivity relationship worked better before the inclusion of the zeroth-order correction term (eq 5). This result is probably due to the presence of the room-temperature-region crossover in the zeroth-order isotope effect. As the temperature dependence of a kie reflects the nature of the force fields used in the calculation, a change in initial geometry or force constants may shift the crossover point. This shift may or may not change the sign of the ln (f^0 ratio) correction term. Thus, one cannot place much confidence in the application of the correction factor in this case. However, even with this problem, the errors involved in the ln (f ratio) additivity for this case are not significantly larger than those for the SN1 and β-elimination models. The presence of the crossover in the room-temperature region should not have a large effect on the zeroth-order intercept correction; a small shift in crossover temperature will change the magnitude of ln A_t^0 but not its sign. As with the previously discussed cases, the intercept additivity relationship required the inclusion of the zeroth-order correction term (eq 6). The errors are again within the range of expected experimental errors.

α-D_2 Substitution in SN2 Model Reactions ("N" Cases). The "N" zeroth-order isotope effect is, as expected, large and inverse [ln (f^0 ratio) ≈ −0.44]. Its temperature dependence is regular. All of the individual force-constant changes investigated represent decreases from reactant to transition state. Thus, as the individual force-constant changes were made larger in magnitude, ln (f ratio)$_i$ changed from inverse to normal. The kie's near the region of change from inverse to normal were sometimes characterized by temperature-dependence anomalies (inflection regions, extrema, crossovers[5]), especially those effects due to the imposition of stretching force-constant changes on the zeroth-order model.

Table IX. Additivity Relationships Evaluation for α-D_2 SN2 "C" Models [ln (f ratio) ≈ −0.12]

Composite	Composition code[a]	10^4 ln (f ratio), 300°K: Σ_i[b]	10^4 ln (f ratio), 300°K: Composite	10^4 ln (f ratio), 300°K: Error[c]	10^4 ln A_f: Σ_i[b]	10^4 ln A_f: Composite	10^4 ln A_f: Error[c]	10^4 ln ($\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$)
z-o[d]			21			−69		308
			One-Directional Force-Constant Changes					
A	s1b	−1221	−1237	−16	111	110	−1	322
B	s1b	−1221	−1223	−02	117	116	−1	308
C	s2b	−1242	−1236	06	36	34	−2	308
D	s2b	−1242	−1246	−04	251	250	−1	325
E	s3b	−1263	−1258	05	164	162	−2	319
F	s3b	−1263	−1254	09	161	160	−1	319
G	3b	−1242	−1255	−13	235	233	−2	322
H	3b	−1242	−1238	04	200	197	−3	320
I	2b	−1221	−1229	−08	269	269	0	331
J	2b	−1221	−1218	03	74	70	−4	308
			Two-Directional Force-Constant Changes					
K	s1b	−1221	−1217	04	712	712	0	369
L	s1b	−1221	−1218	03	−104	−103	1	308
M[e]	s2b	−1242	−1248	−06	643	645	2	355
N	s2b	−1242	−1250	−08	−255	−255	0	299
O	s3b	−1263	−1272	−09	−64	−60	4	291
P	s3b	−1263	−1209	54	−69	−95	−26	273
Q	3b	−1242	−1292	−50	152	168	16	331
R	3b	−1242	−1341	−99	432	489	57	339
S	2b	−1221	−1218	03	434	433	−1	352
T	2b	−1221	−1258	−37	192	212	20	308

[a–d] See corresponding footnotes to Table III. [e] High-temperature crossover at ~1700°K.

An attempt was made not to choose, for inclusion in composite models, individual force-constant changes that produced ln (f ratio)$_i$ values falling in this region. However, in several instances stretching force-constant changes producing effects in this region were used, primarily because the anomalous range was so wide.

Results of the additivity relationships evaluation are given in Tables VII and VIII. The errors in both the isotope effect and intercept relationships are significantly larger than for the previously discussed cases, being almost an order of magnitude larger in the case of the normal direction kie [ln (f ratio) ≈ 0.14].

In the inverse case [ln (f ratio) ≈ −0.12] several composite models produced temperature-dependence anomalies, appearing as high-temperature crossovers (crossover temperatures in the 650–1500°K range). Anomalous kie temperature dependences often characterize reactions where concomitant force-constant increases and decreases are operative at the isotopic position(s).[5] (The increases in this case are due to the manner in which the HC···X bending force constants are assigned; see Model Systems section.) The temperature-dependence anomalies for the composite cases do not necessarily correlate with the inclusion of force-constant changes that result in anomalies when individually applied to the zeroth-order model. The additivity relationships errors for the anomalous kie's are not significantly different from those for the regular kie's.

α-D_2 Substitution in SN2 Model Reactions ("C" Cases). The "C" zeroth-order isotope effect exhibits a double crossover (crossover temperatures ~185 and ~385°K), but the zeroth-order corrections are small. The anomalous temperature behavior of the zeroth-order model disappears when all but the smallest additional individual force-constant changes are included. In the few cases where these small force-constant changes were included in a composite model, there was no apparent manifestation.

The results of the additivity relationships evaluation are presented in Tables IX and X. There is a marked improvement over the corresponding "N" cases (Tables VII and VIII), especially for the normal direction kie [ln (f ratio) ≈ 0.14] cases. The additivity relationships work considerably better for models with only one-directional force-constant changes (*i.e.*, all increases or all decreases between reactant and transition state) than for the cases with both force-constant increases and decreases imposed simultaneously. One inverse kie composite model (M) and one normal direction kie composite model (O) produce kie's exhibiting high-temperature crossovers. The temperature-dependence anomaly does not adversely affect the additivity relationships for the inverse kie model but does appear to reduce their validity somewhat for the normal direction kie model.

Unlike the results with the decarboxylation reaction cases, where the zeroth-order effect also exhibited a temperature-dependence anomaly, here both the quantum kie and Arrhenius intercept additivity relationships required the inclusion of the zeroth-order correction terms.

Discussion

Except for application to the SN2 "N" models, the quantum kie and Arrhenius intercept additivity relationships, eq 5 and 6, are obeyed about as accurately as the precision to which the experimental data can be obtained. The poorer agreement for the SN2 "N" models is probably due to the larger magnitudes of both the isotope effect and Arrhenius intercept zeroth-order correction terms. In the SN2 "N" case with composite ln (f ratio) ≈ 0.14 at 300°K, for which the errors were greatest, an additional, related factor probably contributed to the inaccuracy. The ln (f^0 ratio) for this case is −0.44, so that the additional isotope effect needed to produce ln (f ratio) ≈ 0.14 is approximately 0.58. Consequently, the imposed in-

Table X. Additivity Relationships Evaluation for α-D_2 SN2 "C" Models [ln (f ratio) ≈ 0.14]

Composite	Composition code[a]	$10^4 \ln$ (f ratio), 300°K			$10^4 \ln A_l$			$10^4 \ln$
		Σ_i[b]	Composite	Error[c]	Σ_i[b]	Composite	Error[c]	($\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$)
z-o[d]			21			−69		308
			One-Directional Force-Constant Changes					
A	s1b	1379	1376	−03	−332	−332	0	308
B	s1b	1379	1378	−01	−146	−146	0	308
C	s2b	1358	1365	07	−294	−293	1	295
D	s2b	1358	1364	06	−193	−195	−2	308
E	s3b	1337	1344	07	−369	−373	−4	291
F	s3b	1337	1336	−01	−282	−277	5	302
G	3b	1358	1357	−01	−351	−357	−6	299
H	3b	1358	1370	12	−471	−474	−3	288
I	2b	1379	1366	−13	−537	−536	1	273
J	2b	1379	1400	21	−300	−312	−12	308
			Two-Directional Force-Constant Changes					
K	s1b	1379	1376	−03	−43	− 41	2	308
L	s1b	1379	1375	−04	−984	−983	1	230
M	s2b	1358	1363	05	27	26	−1	339
N	s2b	1358	1333	−25	−325	−305	20	308
O[e]	s3b	1337	1500	163	−555	−657	−102	328
P	s3b	1337	1285	−52	−505	−475	30	256
Q	3b	1358	1319	−39	−416	−402	14	322
R	3b	1358	1303	−55	−778	−758	20	265
S	2b	1379	1380	01	−354	−353	1	325
T	2b	1379	1359	−20	−248	−234	14	308

[a–d] See corresponding footnotes to Table III. [e] High-temperature crossover at ~1700°K.

dividual force-constant changes for this case had to be generally much larger than those for the other cases. Simple additivity relationships cannot be expected to hold as well for large perturbations of a system as they do for small perturbations.

The quantum kie additivity can be examined in the framework of the finite orthogonal polynomial representation of ln (f ratio) developed by Bigeleisen, Ishida, and Spindel.[17–19] Consideration of only the first two sums in the expansion (j = 2 approximation) leads to the conclusion that, for the types of models considered in the present work, the deviations from additivity arise only from terms of the form $f_{ii}f_{kk}(g_{ik,\mathrm{H}}{}^2 - g_{ik,\mathrm{D}}{}^2)$, where i and k represent two *bending* coordinates whose force constants (f_{ii} and f_{kk}) are varied and g_{ik} is the G-matrix[20] (kinetic energy) element for interaction between the two bending motions. Composite j = 2 stretch–bend terms do not lead to deviations from additivity. One would expect, therefore, that the deviations from additivity should be nil for the s1b models and increase with increasing relative bending force-constant change contributions to the kie's. Examination of the numerical results presented in the tables, as well as a detailed analysis of the force fields used in the calculations, indicates that a qualitative trend of this sort exists. A similar trend exists for the Arrhenius intercept additivity. Although no simple theoretical correlation can be made between ln A_l and force-constant changes, the latter trend is not surprising in view of the fact that the bending force-constant changes affect mainly low-lying vibrational frequencies, such frequencies being the major contributors to curvature in kie Arrhenius-type plots. What is surprising is that the ln (f ratio) and ln A_l additivity relationships are obeyed *simultaneously* by room-temperature region data.

The good agreement observed for the quantum kie and Arrhenius intercept additivity relationships suggests a systematic method of fitting model calculations to experimental secondary deuterium kie data. The method is essentially as follows. Reactant geometry and force field and transition-state geometry are chosen; none of these is critical. A "zeroth-order" transition-state force field is chosen with force constants involving the isotopic position(s) as close to the corresponding reactant force constants as possible. In cases where the isotopic position(s) is involved in a different number of internal coordinates in reactant and transition state, the zeroth-order transition-state force constants should be adjusted to make the *net* force-constant change at the isotopic position(s) as close to nil as possible. A zeroth-order kie and Arrhenius fit calculation is carried out to provide values of ln (f^0 ratio) (at a particular temperature) and ln $A_l{}^0$, the zeroth-order correction terms, and an estimate of ln ($\nu_{HL}^{\ddagger}/\nu_{DL}^{\ddagger}$), the classical, infinite-temperature limit to the kie. Each kind of transition-state force constant of interest is varied independently in a stepwise fashion and calculations are carried out to obtain values of individual ln (f ratio)$_i$'s and ln $A_{l,i}$'s. (All of these calculations, including the zeroth-order calculation, can be carried out at the same time; there is no interdependence except, perhaps, in determining the maximum individual force-constant changes to be considered.) A plot of individual ln $A_{l,i}$ *vs.* ln (f ratio)$_i$, such as the one shown in Figure 4, is prepared. A set(s) of points on the curves (zero or one point per curve) is chosen[21] such that the sum of the ordinate

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(17) J. Bigeleisen and T. Ishida, *J. Chem. Phys.*, **48**, 1311 (1968).

(18) T. Ishida, W. Spindel, and J. Bigeleisen, *Advan. Chem. Ser.*, No. **89**, 192 (1969).

(19) J. Bigeleisen, T. Ishida, and W. Spindel, *J. Chem. Phys.*, **55**, 5021 (1971).

(20) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

(21) The selection of points on the curves can be carried out by "brute force" or by fitting polynomials to the curves and solving simultaneous equations. Alternatively, the selection of points can be made by a simple geometric construction method which utilizes the fact that the coordinates of the center of mass of the n points (taken as of equal mass) are n^{-1} times the desired abscissa and ordinate value sums.

values equals

$$\ln A_{\text{obsd}} - \ln(\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}) + (n - 1)\ln A_f^0$$

where n is the number of points in the set, and the sum of the abscissa values equals

$$\ln(k_{\text{H}}/k_{\text{D}})_{\text{obsd}} - \ln(\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}) + (n - 1)\ln(f^0 \text{ ratio})$$

The composite model constructed by combining the transition-state force constants corresponding to the chosen points should simultaneously reproduce the observed kie at the reference temperature and the observed Arrhenius preexponential factor. Small adjustments can be made on the final model in order to make the fit more exact.

When only two kinds of force-constant changes are permitted in the composite model, those force-constant changes are uniquely determined (aside from the final adjustments) by the necessity of fitting both the observed kie and A factor.[22] For reactions where preliminary mechanistic considerations allow n possible kinds of force-constant changes at the isotopic position(s), $n - 2$ must be fixed before the remaining two can be determined. Thus, the proposed systematic method of force-field fitting, although much less arbitrary than trial and error methods, does not necessarily uniquely determine the transition-state force field. However, it does limit the possibilities to which final mechanistic considerations must be applied. Usually, other mechanistic considerations allow one to fix a range for at least one type of force-constant change. Then graphs such as Figure 4 enable one at least to bracket the changes in the other force constants.[23]

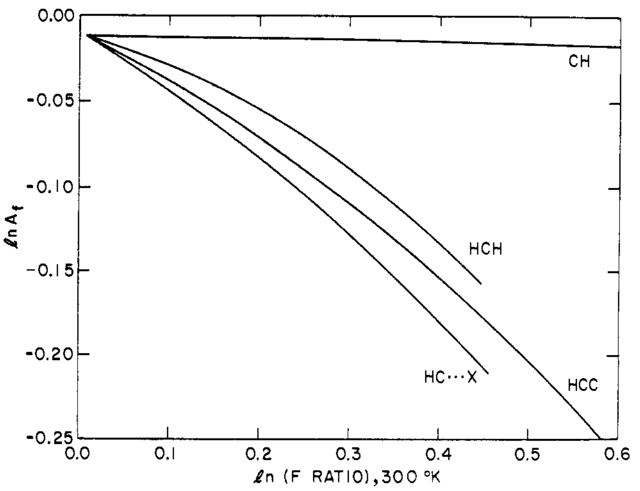

Figure 4. Plot of Arrhenius intercept *vs.* quantum kinetic isotope effect for α-D_2 S_N1 models.

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(22) For certain unusual and fortuitous combinations of curves and observed values, the determination of the two points may not be unique.

(23) The fairly close transferability of the slopes of plots of $\ln A_f$ *vs.* $\ln$ (f ratio) among the different model reaction types prompted us to attempt the development of a simple method of using experimental Arrhenius preexponential factors to gain limited mechanistic information without carrying out detailed model calculations. Our efforts resulted in a method which provided reliable information as to the relative magnitudes of the stretching and bending force-constant change contributions to an isotope effect *only* if f^0 ratio, A_f^0, and $\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}$ were known accurately. As f^0 ratio and A_f^0 are strictly theoretical quantities and there is, at present, no way to extract $\nu_{\text{HL}}^{\ddagger}/\nu_{\text{DL}}^{\ddagger}$ from experimental data in the room-temperature region, we do not feel that the method warrants further exploration.

Ion–Molecule Reactions and the Proton Affinities of the Nitroalkanes. I. Nitromethane and Nitroethane

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Abstract: Ion cyclotron single and double resonance techniques have been used to study the positive ion–molecule chemistry of nitromethane and nitroethane. The reactions in nitromethane can be divided into four classes: (1) proton transfer to nitromethane; (2) methyl cation transfer from CH_3NO^+ and $CH_3NO_2^+$ to nitromethane; (3) NO^+ transfer from $CH_2NO_2^+$; and (4) an unusual O^- abstraction by methyl cation. The reactions in nitroethane are (1) proton transfer to nitroethane from $C_2H_3^+$, H_3CN^+, and $C_2H_5^+$; (2) NO^+ transfer from $H_2NO_2^+$; and (3) a probable dissociation of protonated nitroethane into $H_2NO_2^+$ and C_2H_4. Deuterium and nitrogen-15 isotopic labeling were used to obtain information on the mechanisms of the reactions. Proton transfer reactions were used to determine that the proton affinity of nitromethane is 180 ± 4 kcal/mol while that of nitroethane is 185 ± 4 kcal/mol. These values correspond to $\Delta H_f(CH_3NO_2H^+) = 168$ and $\Delta H_f(C_2H_5NO_2H^+) = 157$ kcal/mol.

The mass spectra of the nitroalkanes are unusual in that the major peaks are hydrocarbon ions. Only the nitromethane ion is stable with respect to decomposition into an alkyl cation and nitrogen dioxide; no significant molecular ion peaks are observed for any other nitroalkane.[2] This behavior can be understood by considering the electronic structures of the nitroalkanes and their molecular ions. The nitrogen atom in the neutral I already has a formal positive

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(2) R. T. Alpin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 87, 4888 (1965).