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Isotope Chemistry and Molecular Structure. A Simplified Theory of End Atom Isotope Effects[1]*

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Abstract: A simple theory for the calculation of isotope effects, applicable to end atom substitution, is developed from the finite orthogonal polynomial method of Bigeleisen and Ishida. It is shown that it is possible to calculate the absolute reduced partition function ratio, at room temperature and above, for end substituted isotopic molecules with reasonable accuracy simply from atomic masses and stretching and bending force constants. The method, which is a simple first order calculation, yields directly the relative importance of bending and stretching forces to the isotope effect as a function of the temperature. It does not require solution of the secular equations for the molecular vibrations. It is particularly suited for the study of end atom isotope effects in homologous compounds. The method is illustrated by the comparison of the new simplified method with exact calculations of the deuterium isotope effects in methane, ethane, and benzene and ^{18}O substitution in formaldehyde.

The development of the finite orthogonal polynomial expansion method for the calculation of the Bigeleisen–Mayer function affords a quantitative and direct method to relate isotope chemistry to molecular forces.[3] Extensive computations[4] of the contributions of individual coordinates, *e.g.*, stretching and bending motions, to the absolute value of $\ln (s/s')f$ and to each of the terms in the expansion

$$\ln (s/s')f = \sum_{j=1}^{n} W_j A_j \sum_{i}^{3n-6} \delta u_i^{2j} \qquad (1)$$

show that there is remarkable additivity, even at room temperature, of the individual coordinates to $\ln (s/s')f$, when the isotopic substitution is at an end atom, *e.g.*, CH_3D *vs.* CH_4, $H_2C^{18}O$ *vs.* $H_2C^{16}O$. This is not true for central atom substitution, $^{13}CH_4$ *vs.* $^{12}CH_4$. At high temperature strict additivity of all forces holds as a consequence of the relationship

$$\ln (s/s')f \cong W_1 A_1 \sum^{3n-6} \delta u_i^2 = W_1 A_1 \left(\frac{\hbar}{kT}\right)^2 \sum_i \sum_j \delta g_{ij} f_{ij} \qquad (2)$$

In eq 2 f_{ij} are the elements of the Wilson **F** matrix and $\delta g_{ij} = g_{ij}' - g_{ij}$ are the differences in those **G** matrix elements which change on isotopic substitution. A_1 is the Wigner coefficient 1/24, $\delta u_i^2 = u_i'^2 - u_i^2$, and W_1 are the finite orthogonal modulating coefficients defined[3] and tabulated[5] previously. We use the Bigeleisen–Mayer convention; the light isotope carries the prime superscript and thus $\ln (s/s')f$ is positive for all real molecules at all temperatures. The coefficient W_1 approaches unity as T, the temperature, goes to infinity. An example of the additivity relationship is given for D substitution in methane in Table I.

The result obtained in Table I is a consequence of

Table I. Major Contributions to $\ln (s/s')f$ in CH_3D/CH_4

	Absolute value	C–H stretch	H–C–H bend
f_{ij}, mdyn Å^{-1}		5.495	0.475
δg_{ij}, amu (and z^a)		0.496 (1)	0.496 (3)
T = 300°K	2.4562	71.2%	30.3%
760[b]	0.66096	75.8	24.5
3020[b]	0.053756	79.1	20.9
∞		79.4	20.6

[a] Number of equivalent internal coordinates with $\delta g \neq 0$. [b] 760°K = $\theta_{max}/2\pi$, and 3020°K = $\theta_{max}/(\pi/2)$.

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

(4) J. Bigeleisen, R. Hom, and T. Ishida, papers in preparation.

(5) Document NAPS 01022, National Auxiliary Publication Services, CCM Information Corp., New York, N. Y. 10022.

Table II. Simplified Direct Method of Calculating ln $(s/s')f$ (T = 300°K)

Molecule	Bond type	ν, cm^{-1}	μ'	W_i'	μ	W_i	$f_{ii}{}^b$	Contribution to ln $(s/s')f$
CH_4[a]	C—H stretch	3145	1	0.485	$^1/_2$	0.600	5.495	1.651
	3 × HC—H bend	1360	1	0.771	$^1/_2$	0.771	0.475	0.892
	μ_j term							−0.086
								Σ = 2.457
								Exact[d] = 2.321
C_2H_6[a]	C—H stretch	2900	1	0.506	$^1/_2$	0.633	4.703	1.444
	1 × H—C—C bend	1200	1	0.805	$^1/_2$	0.805	0.506	0.331
	2 × H—C—H bend	1385	1	0.760	$^1/_2$	0.760	0.452	0.558
	μ_j term							−0.081
								Σ = 2.252
								Exact = 2.353
C_6H_6[a] planar	C-H stretch	3050	1	0.495	$^1/_2$	0.614	5.063	1.546
	Wag	1200	1	0.805	$^1/_2$	0.805	0.870	0.569
	μ_j term							−0.082
								Σ = 2.033
								Exact = 2.144
			g'		g			
CH_2O[c] $^{18}O/^{16}O$	C═O stretch	1770	0.14585	0.687	0.13889	0.687	12.7	0.0992
	2 × H—C═O bend	1200	1.06354	0.805	1.05883[c]	0.805	0.827	0.0102
								Σ = 0.109
								Exact = 0.0904

[a] Equation 6, $\ln (s/s')f = (1.625)\,[\Sigma(W_i'\mu_i' - W_i\mu_i)f_{ii} + (W_i' - W_i)\mu_j f_{ii}]$. [b] All force constants in mdyn Å^{-1}. [c] Equation 5, $W' = W$. [d] Exact corresponds to the exact calculation of ln $(s/s')f$ with the same **F** matrix.

the fact that eq 2 is good to about 10% for the calculation of ln $(s/s')f$ at room temperature and the general structure of **G** matrices when one uses internal coordinates. Inspection of the general rules for the construction of **G** matrices[6] shows that only diagonal elements, stretch and bend, and the off-diagonal bend–bend elements have nonzero δg_{ij} elements for end atom isotopic substitution. From this and eq 2 it follows directly that isotope effects for end atom substitution will be additive in the internal coordinates for end atom substitution within the validity of eq 2.

Insofar as we are concerned with the motion of an end atom in a polyatomic molecule, the internal coordinates are a good approximation to the normal coordinates. For instance the stretching motion does not couple with the bending motion. However, there is usually extensive coupling of the internal bending coordinates among themselves and with the rotation of the molecule. Fortunately, bending motions make a contribution of less than $^1/_3$ to the total value of ln $(s/s')f$ and a small error in estimating their contribution is of minor importance.

We are, therefore, led to suggest a very simple method for estimating ln $(s/s')f$ directly from **F** and **G** matrix elements which provides significant insight into the relative contributions of the different coordinates. We write

$$\ln (s/s')f = \sum_i^{3n-6} [\ln b(u_i') - \ln b(u_i)] \tag{3}$$

where

$$\ln b(u_i') \cong W_i'(u_i')A_1(\hbar/kT)^2\lambda_i' \tag{4}$$

and λ_i is $4\pi^2\nu_i^2$. Thus

$$\ln (s/s')f \cong 1/24(\hbar/kT)^2\Sigma(W_i'g_{ii}' - W_ig_{ii})f_{ii} \tag{5}$$

where W_i' and W_i, the first-order modulating coefficients, are evaluated at u_i' and u_i, respectively.

Inasmuch as we shall use only first-order modulating coefficients, we have abbreviated the notation W_{1i}' and W_{1i} to W_i' and W_i, respectively. For stretching coordinates we assume

$$\lambda_i \cong (\mu_i + \mu_j)f_{ii}$$

where μ_i and μ_j are respectively the reciprocals of the atomic masses of the isotopic atom and the atom connected by the stretching coordinate. This assumption and the value of T suffice to estimate W_i' and W_i for the stretching modes. For the bending modes the assumption $W_i' \simeq W_i$ is adequate. The bending modes are soft and W is a slow function of u at low u. Further, the absolute differences in u_i' and u_i are small for bending modes compared with stretching modes. The values of W for the bending modes can thus be estimated from approximate vibrational spectral assignments. We obtain under these assumptions

$$\ln (s/s')f \cong 1/24(\hbar/kT)^2 \sum_i^{3n-6} [W_1'\mu_i' - W_i\mu_i)f_{ii} + (W_i' - W_i)\mu_jf_{ii}(\text{stretch})] \tag{6}$$

where the second term in the brackets applies to the stretching coordinates only. In Tables II and III we illustrate the application of eq 6 to D substitution in CH_4, C_2H_6, and C_6H_{12} and eq 5 to ^{18}O substitution in CH_2O at 300°K and at the reduced temperatures $u_{\max} = 2\pi$. For stretching motions we assume

$$W_D(u_D) = W(u_H/\sqrt{2})$$

The term

$$1/24(\hbar/kT)^2(W_i' - W_i)\mu_jf_{ii} \simeq -7470/T^2 \tag{7}$$

for H–D substitution when H is bound to carbon. For heavy atom isotope effects $W' \cong W$ and the term given by (7) can be neglected. We see that eq 6 provides a

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

Table III. Simplified Direct Method of Calculating ln $(s/s')f$ at $T = (\theta_{max}/2\pi) = (h\nu_{max}/2\pi k)$

Molecule and temp	Bond type	ν, cm^{-1}	μ'	W_i'	μ_i	W_i	f_{ii}	Contribution to ln $(s/s')f$
CH$_4$	C—H stretch	3145	1	0.796	$^1/_2$	0.878	5.495	0.496
760°K	3 × H—C—H bend	1360	1	0.948	$^1/_2$	0.948	0.475	0.171
	μ_j term							−0.009
								Σ = 0.658
								Exact = 0.661
C$_2$H$_6$	C—H stretch	2900	1	0.805	$^1/_2$	0.883	4.703	0.481
720°K	1 × HCC bend	1200	1	0.955	$^1/_2$	0.955	0.506	0.068
	2 × HCH bend	1385	1	0.940	$^1/_2$	0.940	0.452	0.120
	μ_j term							−0.009
								Σ = 0.660
								Exact = 0.662
C$_6$H$_6$	C—H stretch	3050	1	0.825	$^1/_2$	0.897	5.063	0.424
planar	Wag	1200	1	0.965	$^1/_2$	0.965	0.870	0.094
810°K	μ_j term							−0.007
								Σ = 0.511
								Exact = 0.514
			g'		g			
CH$_2$O	C=O stretch	1770	0.14585	0.906	0.13889	0.906	12.7	0.0240
^{18}O/^{16}O	2 × HC=O	1200	1.06354	0.952	1.05883	0.952	0.827	0.0022
700°K								
								Σ = 0.0262
								Exact = 0.0248

rapid estimate of ln $(s/s')f$ valid to within 10% at 300°K and correspondingly better at higher temperatures. We note that our approximate calculations, by eq 5, of ln $(s/s')f$ for $CH_2{}^{18}O/CH_2{}^{16}O$ are consistently higher than the exact values. This is a consequence of the kinetic energy coupling term, which is of importance when the isotopic atom, O, is bonded to a lighter atom or one of comparable mass, C. This kinetic energy coupling term appears to first order in the term $W_2A_2 \cdot (\hbar/kT)^4\Sigma\delta u_i{}^4$ and cannot be simply corrected for by adjustment of the modulating coefficient W_1. The sign of A_2 is negative; all other quantities are positive.

From Tables II and III we can get good approximations of the relative importance of the stretching and bending motions as a function of the temperature. These are compared with exact calculations in Table IV.

Table IV. Percentage Contribution of Bending Force Constants to ln $(s/s')f$ as a Function of Temperature

Molecule	T = 300°K		$\theta_{max}/2\pi$		∞
	Eq 6	Exact^a	Eq 6	Exact^a	
CH$_3$D/CH$_4$ H—C—H	36	30	26	25	21
C$_2$H$_5$D/C$_2$H$_6$					
H—C—H	25	20	18	17	15
H—C—C	15	12	10	10	8
C$_6$H$_5$D/C$_6$H$_6$ (in plane) H—C—C	28	27	18	18	15
CH$_2{}^{18}$O/CH$_2$O H—C=O	9.4	9.4	8.4	8.5	8.0

^{a} Unpublished calculations of Bigeleisen and Ishida.

The computational time required to carry out the exact calculations of the relative contributions of stretching and bending motions even on a CDC 6600 computer for a molecule as simple as CH$_4$ is not trivial, primarily because such effects are calculable only by means of an extrapolation procedure, which requires solution of several secular problems.[4] The present method thus provides a good simple method for both estimating the absolute value of ln $(s/s')f$ and the relative importance of different modes for end atom substitution. The method is applicable at all temperatures and applies equally well to deuterium and heavy atom isotope effects.

All of our previous applications of the finite orthogonal polynomial method[3] were such as to take advantage of the exact mathematical properties of $\Sigma\delta u_i{}^{2j}$. These lead to such important theorems as the rule of the mean, the equivalence of isomers, etc.[7] To obtain ln $(s/s')f$ as a series of $\Sigma\delta u_i{}^{2j}$ it is necessary to have the same W_j for all u_i and u_i' of the system under investigation. This can be done by the choice of $W = W(u')_{max}$. This choice satisfies the convergence requirement. It also avoids the requirement of a detailed knowledge of the individual eigenvalues. The present application utilizes individual, but exactly calculable W factors, for the stretching and bending coordinates. It suffices to utilize known data on vibrational frequencies to approximate the W's to be able to get a good estimate of the relative contributions of the stretching and bending forces to ln $(s/s')f$ as a function of the temperature by eq 6.

The temperature dependence of the relative importance of stretching and bending motions appears in first order from the $W_2A_2\Sigma\delta u_i{}^4$ term when one uses eq 1. By using individual W factors, eq 6, we can get the temperature coefficient of the relative contributions directly from the first order term. Equation 6 should also be useful in correlating changes in isotope effects in a homologous series, where a large part of the effect remains constant, *e.g.*, CD$_3$F, CD$_3$Cl, CD$_3$Br, and CD$_3$I compared with CH$_3$F, CH$_3$Cl, CH$_3$Br, and CH$_3$I, respectively. In this series the important change is the H-C-X bending force constant, while the C-H stretching and H-C-H bending force constants remain relatively constant.

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