TTP): the $M(NTP-H)^{3-}$ species also occur in "open" and "closed" forms. In several M^{2+}/NTP systems[47,48] all these different complexes must exist simultaneously in the physiological pH range.

To conclude, the versatility of the interactions of nucleotides with surrounding ions and molecules is indeed impressive; they form hydrogen bonds and stack with each other as well as with other species; their coordinating properties are truly ambivalent: they offer not only different binding sites for different metal ions but also change their ligating qualities toward the same metal ion as the concentrations change. At low concentrations isomeric equilibria exist involving macrochelates, while at higher concentrations metal-ion-bridged stacks of dimers may be formed. Moreover, it appears that all these properties may be combined in several ways to create additional properties—here exists obviously a huge reservoir to achieve selectivity, and indeed nucleotides are involved in some of the most selective processes occurring in nature.

Acknowledgment. We thank Mr. K. Aegerter for recording the 90-MHz NMR spectra, the CIBA-Stiftung Basel for support toward the costs of these spectra, and the Swiss National Science Foundation for a research grant.

Nonpotential Energy (NPE) Effects in Organic Chemical Reactions: Development of a Suitable Force Field

Christine D. Chalk, Barrie G. Hutley, James McKenna,* Leslie B. Sims, and Ian H. Williams

Contribution from the Department of Chemistry, The University, Sheffield S3 7HF, England.

Received December 6, 1979

Abstract: A preliminary analysis is given of the role of NPE effects in organic chemistry. Calculation of these effects centers around a vibrational analysis program based on a suitable force field. A simple valence force field (SVFF) is chosen for the purpose, initially on the basis of a limited range of molecular types (alkanes and alkyl halides) but capable in principle of extension as required. Special weighting is given to accurate reproduction of the entropy-rich lower frequencies, and particular attention is paid to analysis of torsional force constants and torsional frequencies.

Introduction

Most interpretations of equilibria or reactivities in organic chemistry have traditionally been made on the basis of potential energy changes (bond energies, resonance energies, aromaticity or antiaromaticity, strain energies, coulombic aspects of solvation, etc.) with little or no attention being paid to contributions from other (nonpotential energy (NPE)) effects, apart from occasional usually rather qualitative interpretations of entropy changes where these are experimentally available and relatively large, and treatment of kinetic isotope effects. A more general analysis of NPE effects seems desirable, particularly since such contributions seem likely to be substantial for many reactions in solution, including enzyme-catalyzed processes.[1] In this paper we describe the development of a suitable force field for such analysis, and in accompanying papers we deal with calculations of NPE effects and related kinetic isotope effects for some nucleophilic substitutions and 1,2-eliminations. These calculations apply strictly to ideal gas conditions; in the future we shall report on solvation effects and simple enzyme models where the calculated NPE effects are, as expected, very much larger.

The expression "nonpotential energy" which we abbreviate to "NPE" suffers from an obvious negative character, but it is nevertheless both comprehensive and unambiguous, and it seems preferable to various other designations which are inadequate, incomplete, or otherwise objectionable for one reason or another: for example, mass, "ponderal",[2] or partition function (effects). Nonpotential energy effects, as defined, do of course depend on the topography of the relevant potential energy surfaces.

The drawbacks of overemphasis of potential energy interpretations in organic chemistry were recognized by Hammett, who in his classical text (1940) on physical organic chemistry wrote[3] that "any approach to the effect of structure upon equilibrium or heat of reaction that treats a molecule as a rigid lifeless structure can be no more than the crudest approximation". He might equally well have commented on similar interpretations of rate constants. Conventional discussions of equilibria or reactivity dealing only, and usually implicitly, with potential energy changes refer just to the behavior of molecules at absolute zero which have lost not only their thermal energies but also, more mysteriously, their zero-point energies, perhaps by the intervention of a Maxwell demon!

A very considerable improvement in interpretation is of course effected when free energies of reaction or of activation are determined and separated into enthalpy and temperature-entropy effects (eq 1). While such analyses are conveniently based on

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

experimental measurement of the temperature coefficients of equilibrium or rate constants, there are nevertheless some drawbacks. First, the potential energy change, which chemists are so interested in interpreting, if usually implicitly rather than explicitly, is not specifically isolated. This term is not of course equivalent to the enthalpy change, although it is often by implication assumed to be so. Second, the enthalpy and entropy changes are both dependent on partition-function changes in a way which causes a degree of opposition between the two. Third, there is no isolation of zero-point energy changes, which correspond to perhaps the most unknown territory of all in the whole region of analysis of reactivities and equilibria.

A free energy change ΔG may be expressed[1] by eq 2 in which $\Delta\epsilon$, ΔE_{zp}, ΔE_{th}, and $P\Delta V$ represent changes in potential energy, zero-point energy, thermal energy, and pressure–volume terms, respectively; these terms together constitute an enthalpy change

---

(1) D. B. Cook and J. McKenna, *J. Chem. Soc., Perkin Trans 2*, 1223 (1974).

(2) C. K. Ingold, *Q. Rev., Chem. Soc.*, **11**, 1 (1957).

(3) L. P. Hammett, "Physical Organic Chemistry"; McGraw-Hill, New York, 1940, p 76.

as in eq 1. The zero-point energy term is given simply by changes

$$\Delta G = \Delta\epsilon + \Delta E_{zp} + \Delta E_{th} + P\Delta V - T\Delta S \qquad (2)$$

in vibrational frequencies; the thermal energy and temperature-entropy terms are determined by the partition functions q' for the reactants and q'' for the products (or transition state), as given by eq 3 and 4. A superior analysis of free energy changes is

$$\Delta E_{th} = RT^2 \, d \ln (q''/q')/dt \qquad (3)$$

$$T\Delta S = RT \ln (q''/q') \qquad (4)$$

provided on the basis of eq 2, where potential energy changes $\Delta\epsilon$ are separated from NPE changes $\Delta(G - \epsilon)$, and although neither of these quantities may be evaluated directly by experiment, each may in principle be obtained by calculation. Equation 2 can of course be applied to free energies either of reaction or of activation.

A satisfactory program for vibrational analysis is central to any general scheme for calculation of NPE effects in organic reactions. It is well-known that contributions to molecular partition functions from vibrational motions are very small as compared to contributions from translational and rotational motions. Thus, although it is recognized that translational and rotational motions may exercise very considerable effects on rate or equilibrium constants as exemplified, for instance, by the entropic differentiation between intra- and intermolecular reactions, vibrational motions are commonly regarded as being unimportant in such considerations. While this assumption may often be valid, there are certainly cases where it is not: these may arise when equilibrium (or rate) constants are determined by small free energy differences between reactants and products (or transition states) or when reactions involve changes in modes of vibration having very low frequencies. The fact that vibrational entropies and zero-point energies may not safely be ignored in considerations of small conformational free energy differences for substituted cyclohexanes has been noted by Reisse,[4] and one of us has suggested[1] that vibrational activation entropy, arising from changes in very low-frequency vibrational modes, may be of potential importance in enzyme catalysis.

Of course, isotope effects are familiar manifestations of NPE contributions in reactivity and equilibria, and these have been studied extensively. However, the consequences of the presence and distribution of *vibrationally structured mass* in reacting systems have not previously been investigated to any appreciable extent.

Program

In all our work we have used a Fortran computer program QREL which performs calculations of normal coordinates and of NPE contributions to free energies and to rate and equilibrium constants. For any molecular species the partition functions of translational, rotational, vibrational, and free internal rotational motions may be calculated as required by using standard (gas-phase) expressions of statistical thermodynamics within the rigid rotor/harmonic oscillator approximation, and these are used to obtain values of thermodynamic functions including $(G^\ominus - \epsilon)$, E_{zp}, $(H - \epsilon)$, and $S^\ominus$, the superscripts referring to defined standard states. For any reaction a rate or equilibrium constant may be calculated from the values of $(G^\ominus - \epsilon)$ for reactants and transition state or products, and similarly a relative rate or equilibrium constant may be obtained for any pair of reactions. Potential energetic contributions may also be input to calculations by using QREL but have been deliberately omitted in all work presently reported.

Input of a molecular force field to QREL simply requires specification of individual internal coordinates and their associated force constants. In particular, the treatment of torsional vibrations by QREL requires only a very simple data input: for any torsional vibration just the atoms defining the bond about which the torsion occurs are specified together with a single force constant; a completely general method[5] of torsional coordinate specification is used which is applicable to molecules of any geometry or topology. Internal coordinates are transformed by QREL into Cartesian coordinates by using analytical forms for the necessary derivatives, and normal coordinates are found by diagonalization of the matrix of force constants in mass-weighted Cartesian coordinates.[6] Calculated frequencies may be compared with observed frequencies and various errors computed for each mode.

Development of a Model Force Field

An accurate description of the potential energy surface of a molecule would enable many different properties to be calculated consistently, including partition functions. Empirical force fields are commonly used to model potential energy surfaces but with few exceptions[7] are designed to reproduce only a particular set of molecular properties such as vibrational frequencies[8] or geometries and strain energies.[9] Our requirement is for a model force field for use in calculations of vibrational partition functions by the standard harmonic oscillator expression (5) in which ν_i is

$$q_{vib} = \prod_i [1 - \exp(-hc\nu_i)/kT]^{-1} \qquad (5)$$

the frequency (in cm^{-1}) of the ith normal mode. Since this expression has an inverse exponential dependence on frequency, the contribution from each mode increases greatly as the frequency decreases, and therefore it is clear that accurate evaluation of the vibrational partition function requires accurate estimation of low frequencies of vibration. In the absence of any published force field satisfactorily fulfilling these requirements we have chosen to develop a model force field which enables vibrational frequencies and thence partition functions to be calculated within the harmonic approximation in which special emphasis is given to the reproduction of low-frequency vibrational modes of particular importance in determining the vibrational entropy.[1] Calculation of molecular vibrational frequencies may be achieved by computation of force constants subsequent to optimization of geometry by means of either empirical[7] or quantum mechanical[10] methods. Although in principle it is desirable to use optimized geometries in normal-coordinate calculations, such procedures involve relatively lengthy and costly computations but do not necessarily generate frequencies of sufficient accuracy for our purposes to justify their use. For reasons of simplicity and ease of use we have adopted a simple valence force field (SVFF) using idealized geometries as the basis for an empirical model, since it is our intention to perform calculations of NPE contributions to the reactivity of large and complex molecular systems for which more sophisticated methods would be impractical. In this paper we describe a model SVFF developed for calculations of spectroscopic and most particularly thermodynamic quantities for a range of simple alkanes, chloroalkanes, and bromoalkanes in order to demonstrate the validity of this approach. This force field may clearly be extended as required to cover wider ranges of molecules.

In a SVFF the potential energy V is given by eq 6, where the

$$V = \tfrac{1}{2} \sum_i F_{ii}(\Delta R_i)^2 \qquad (6)$$

summation is over changes in all the internal coordinates and ΔR_i and the F_{ii} are the (so-called diagonal) force constants. We assumed idealized geometries by using standardized bond lengths and setting all interbond angles equal to the tetrahedral angle. In order to reduce the number of parameters in the force field to a minimum, we constrained force constant values to be

---

[4] J. Reisse in "Conformational Analysis: Scope and Present Limitations", G. Chiurdoglu, Ed., Academic Press, New York, 1971, pp 219–228.

(5) (a) I. H. Williams, *J. Mol. Spectrosc.*, **66**, 288 (1977); (b) I. H. Williams, J. McKenna, and L. B. Sims, *J. Mol. Struct.*, **55**, 147 (1979). See this reference for information about program availability.

(6) (a) W. D. Gwinn, *J. Chem. Phys.*, **55**, 477 (1971); (b) H. L. Sellers, L. B. Sims, L. Schäfer, and D. E. Lewis, *J. Mol. Struct.*, **41**, 149 (1977).

(7) (a) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5118 (1968); (b) A. Warshel and S. Lifson, *ibid.*, **53**, 582 (1970); (c) O. Ermer, *Struct. Bonding (Berlin)*, **27**, 161 (1976).

(8) J. L. Duncan, *Mol. Spectrosc. (Chem. Soc., London)*, **3**, 104–162 (1975).

(9) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976).

(10) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).

transferable within the range of molecules considered; however, in recognition of the fact that the values of diagonal force constants corresponding to formally identical atomic groupings depend on the particular local environments of those groupings, we required that force constants took the same values only when corresponding to the same formal atomic groupings within equivalent local environments. Judicious selection of transferable parameters allowed a suitably flexible model to be developed.

Force constants for the molecules used in the force field development were adjusted so as to minimize a root-mean-square weighted error W in the frequencies calculated for each molecule; the weighting factor adopted for each mode was the vibrational entropy S_i^{obsd} calculated at $T = 298.16$ K from the observed frequency ν_i^{obsd} (cm^{-1}) by eq 7, where $x_i = hc\nu_i^{\text{obsd}}/kT$ and the error W, given by eq 8, thus suitably emphasizes the importance

$$S_i = R[x_i e^{-x_i}(1 - e^{x_i})^{-1} - \ln(1 - e^{-x_i})] \tag{7}$$

$$W = \left\{ \frac{\sum_i^{3N-6} [(\nu_i^{\text{obsd}} - \nu_i^{\text{calcd}})S_i^{\text{obsd}}]^2}{\sum_i^{3N-6} [S_i^{\text{obsd}}]^2} \right\}^{1/2} \tag{8}$$

of low-frequency modes. Calculated frequencies were assigned by inspection of the eigenvectors for the normal coordinates and of the effects of appropriate force constant changes or isotopic substitutions.

Wherever possible gas-phase spectroscopic data were used for calibration of the force field, but where gas-phase frequencies were unavailable, condensed-phase data and occasionally a calculated frequency were used instead. Phase shifts of low-frequency modes may be very important, since these may be of considerable magnitude,[11] but phase shifts on high-frequency modes would be unimportant for our purposes. Scant attention has previously been given to low-frequency modes in the development of force fields (cf. ref 12).

The sources of the observed frequencies, together with the phase (gas, liquid, solid, or calculation) to which they refer, are specified below for all the molecules used in the force field development.

Methane (T_d): stretching modes, gas;[13] bending modes, gas.[14]

Ethane (D_{3d}): stretching and bending modes, gas;[15] torsional mode, gas.[16]

Propane (C_{2v}): stretching and bending, A_1, B_1, and B_2 modes, gas,[17] and A_2 modes, calculated;[18] torsional modes, liquid.[19]

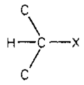
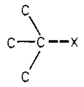
2-Methylpropane (C_{3v}): stretching and bending modes, solid,[20] except the degenerate skeletal bend at 367 cm^{-1}, liquid,[21] and A_2 modes, calculated;[20] torsional modes, gas.[22] (A degenerate E mode is observed in gas and solid, and gas-phase frequency of the A_2 mode is estimated from observed solid-phase frequency by assuming a corresponding frequency shift.)

2,2-Dimethylpropane (T_d): stretching and bending, A_1 and E modes and F_2 bend at 414 cm^{-1}, liquid,[23] other F_2 modes, solid,[20] and unobserved A_1, E, and F_1 modes, calculated;[20] torsional modes, solid.[24] (2,2-Dimethylpropane forms globular molecular crystals, in which there is thought to be rotational freedom, as does 2-chloro-2-methylpropane for which the torsional frequencies are thought to be the same in gas and solid phases.[25])

Table I. Structural Date for Model SVFF

atomic masses, amu		bond lengths, Å	
^{12}C	12.003844	C-C	1.53
^{1}H	1.008145	C-H	1.10
^{35}Cl	34.98006	C-Cl	1.79
^{79}Br	78.943665	C-Br	1.95
interbond angles = $\cos^{-1}(-1/3) = 109.47122°$			

Table II. Bond Stretching Force Constants for Model SVFF

bond	environment	force constants, mdyn Å^{-1}	
carbon-carbon (C-C)	all cases	5.0	
carbon-hydrogen (C-H)	C *not* bonded to a halogen	4.7	
	C bonded to a halogen	4.85	
		X = Cl	X = Br
carbon-halogen (C-X)	H-CH$_2$-X	3.50	2.93
	H$_3$C-CH$_2$-X	2.85	2.01
	H-C$\underline{\text{anti}}$CH$_2$-X	2.50	1.67
	C-C$\underline{\text{anti}}$CH$_2$-X	2.50	2.18
		2.30	2.20
		2.30	2.10

Butane, Anti Conformer (C_{2h}): stretching and bending, A_u and B_u modes above 900 cm^{-1}, solid,[26] A_g and B_g modes above 1460 cm^{-1}, solid,[27] A_g and B_g modes at 1053, 1148, 1300, and 1455 cm^{-1}, solid,[28] unobserved modes (at 1180, 1361, and 1382 cm^{-1}), calculated,[20] and modes below 900 cm^{-1}, gas,[29] except for the A_u mode at 733 cm^{-1}, solid,[26] torsional modes, solid.[30]

Chloromethane (C_{3v}): all modes, gas.[31]

Chloroethane (C_s): all modes, gas.[32]

2-Chloropropane (C_s): all modes, gas, except the mode at 972 cm^{-1} and torsional modes, liquid.[33]

2-Chloro-2-methylpropane (C_{3v}): stretching and bending, A_1 and E modes, gas,[34] and A_2 modes, calculated;[34] torsional modes, solid.[25] (The frequency of the skeletal bending E mode is the same in the gas phase as in the crystalline phase, and thus the phase shift for the torsional frequencies is thought to be minimal also.[25])

1-Chloropropane, Anti Conformer (C_s) **and Gauche Conformer** (C_1): stretching and bending modes, liquid;[35] torsional modes, gas.[11a]

Bromomethane (C_{3v}): all modes, gas.[36]

---

(11) (a) K. Radcliffe and J. L. Wood, *Trans. Faraday Soc.*, **62**, 1678 (1966); (b) G. E. Campagnaro, I. Haque, C. E. Souter, and J. L. Wood, *Spectrochim. Acta, Part A*, **30A**, 517 (1974).

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

(13) B. P. Stoicheff, C. Cumming, C. E. St. John, and H. L. Walsh, *J. Chem. Phys.*, **20**, 498 (1952).

(14) J. S. Burgess, *Phys. Rev.*, **76**, 302 (1949).

(15) I. Nakagawa and T. Shimanouchi, *J. Mol. Spectrosc.*, **39**, 255 (1971).

(16) S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).

(17) J. N. Gayles, Jr., and W. T. King, *Spectrochim. Acta*, **21**, 543 (1965).

(18) J. N. Gayles, Jr., W. T. King, and J. H. Schachtschneider, *Spectrochim. Acta, Part A*, **23A**, 703 (1967).

(19) E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **40**, 1124 (1967).

(20) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).

(21) J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **34**, 1037 (1956).

(22) J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.*, **53**, 38 (1970).

(23) D. H. Rank, B. D. Saksena, and E. R. Shull, *Discuss. Faraday Soc.*, **9**, 187 (1950).

(24) J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.*, **52**, 2046 (1970).

(25) J. R. Durig, S. M. Craven, and J. Bragin, *J. Chem. Phys.*, **51**, 5663 (1969).

(26) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 85 (1963).

(27) T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **17**, 1102 (1949).

(28) J. K. Brown, N. Sheppard, and D. M. Simpson, *Philos. Trans. R. Soc. A, London, Ser.* **247**, 35 (1954).

(29) A. L. Verma, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **60**, 1540 (1974).

(30) K. W. Logan, H. R. Danner, J. D. Gault, and H. Kim, *J. Chem. Phys.*, **59**, 2305 (1973).

(31) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York, 1945, p 312.

(32) F. A. Miller and F. E. Kiviat, *Spectrochim. Acta, Part A*, **25A**, 1363 (1969).

(33) P. Klaboe, *Spectrochim. Acta, Part A*, **26A**, 87 (1970).

(34) J. C. Evans and G. Y.-S. Lo, *J. Am. Chem. Soc.*, **88**, 2118 (1966).

(35) K. Tanabe and S. Saëki, *J. Mol. Struct.*, **27**, 79 (1975).

(36) H. B. Weissmann, R. B. Bernstein, S. E. Rosser, A. G. Meister, and F. F. Cleveland, *J. Chem. Phys.*, **23**, 544 (1955).

Table III. Valence Angle Bending Force Constants for Model SVFF

atoms defining interbond angle	environment	substituent atom P	force constant, mdyn Å rad^{-2}			
			substituent atom Q			
			H	C	Cl	Br
H-C-H	H-C(P,Q)-H	H	0.518	0.485	0.485	0.485
		C	0.485	0.47	0.40	0.34
C-C-H	C-C(P,Q)-H	H	0.635	0.61	0.57	0.58
		C	0.61	0.68	0.60	0.58
C-C-C	C-C(P,Q)-C	H	0.89	0.96	0.96	1.10
		C	0.96	1.03	1.03	1.17
		conformatn				
	C-C-CH_2-Q	anti		1.228	1.51	1.27
		gauche		0.89	1.04	1.20

atoms defining interbond angle	environment	substituent atom X	P = H Q = H	P = H Q = C	P = C Q = C
H-C-X[a]	H-C(P,Q)-X	Cl	0.74	0.86	0.86
		Br	0.638	0.70	0.70
C-C-X[a]	C-C(P,Q)-X	Cl	1.10	1.17	1.24
		Br	1.19	1.10	1.17

atoms defining interbond angle	environment	conformatn	substituent atom X	
			Cl	Br
C-C-X	C-C-CH_2-X	anti	0.80	0.99
		gauche	1.10	1.19

[a] X = halogen.

Bromoethane (C_s): all modes, liquid,[37] except the skeletal bending mode at 288 cm^{-1} and the torsional mode, gas,[38] and mode at 1131 cm^{-1}, calculated.[39]

2-Bromopropane (C_s): all modes, gas,[33] except torsional modes, liquid.[33]

2-Bromo-2-methylpropane (C_{3v}): stretching and bending, A_1 and E modes, gas,[40a] except for modes at 285, 930, and 1449 cm^{-1}, liquid,[40a] and A_2 modes, calculated;[40a] torsional modes, solid.[25]

1-Bromopropane, Anti Conformer (C_s) and Gauche Conformer (C_1): stretching and bending modes, liquid;[35] torsional modes, gas.[11a]

The values of atomic masses, bond lengths, and interbond angles used are given in Table I; only conformations involving perfectly staggered arrangements of substituents about carbon–carbon bonds were considered. Tables II and III contain force constant values for stretching and bending coordinates, respectively. The force constants for bending of angles subtended at an apical atom by two terminal atoms depend either upon the nature and degree of the substitution at the apical atom or upon the nature and position of substitution at a terminal atom. Thus the force constant for bending of a CCC angle tends to increase from its value in propane as the apical atom is substituted by a halogen or by additional carbon atoms or as one of the terminal atoms is similarly substituted in a position either anti or gauche to the other terminal atom. Table IVa contains values of torsional force constants for all the molecules used in the force field development.

Calculations of Vibrational Frequencies

The model SVFF perform well in the reproduction of vibrational frequencies for the molecules used in its development, although it tends to fail in cases where strongly coupled modes are involved. For example, the degenerate methyl rocking modes in ethane at 883 cm^{-1} are calculated too high but are strongly coupled to another pair of like modes at 1069 cm^{-1} which are calculated too low (observed 821 and 1183 cm^{-1}); an interaction force constant coupling the HCC bending coordinates of each antiperiplanar four-atom chain, HCCH, would be needed to improve the calculation. Similarly the torsional frequencies for propane are calculated at 228 and 251 cm^{-1} whereas the corresponding observed frequencies are more widely separated at 216 and 271 cm^{-1} and could be reproduced if an interaction force constant were included in the calculation.[5a] The SVFF seeks to calculate the frequencies of pairs of coupled modes such that the error in the vibrational entropy of the two modes is minimized. The error P in the total vibrational entropy for each molecule is calculated from eq 9, where S^{obsd} and S^{calcd} are entropies at 298.16 K computed on the basis of observed and calculated frequencies, respectively, being the sum of contributions S_i from each of the $3N - 6$ vibrational modes.

$$P = [(S^{\text{obsd}} - S^{\text{calcd}})/S^{\text{obsd}}]100 \qquad (9)$$

In Table V the results of frequency calculations using the model SVFF are compared with results obtained from published frequencies calculated by using more sophisticated force fields which include some or many interaction force constants and which thus involve more parameters than does the SVFF. The SVFF values and the literature values of calculated frequencies were for each molecule compared with the same set of observed frequencies and were subjected to the same criteria for assessment of performance. The error P in the total vibrational entropy and the entropy-weighted root-mean-square error W in the frequencies are presented, and it may be seen that in most cases the errors resulting from the model SVFF are appreciably lower than those resulting from the published force fields. Most of the errors generated by the published force fields arise from those low-frequency vibrational modes to which little attention had been given by the respective authors; this fact serves to illustrate the value of the specific emphasis on low frequencies in this work, and the results demonstrate the ability of the model SVFF to reproduce these modes satisfactorily. A more conventional test of the performance of a force field is provided by the unweighted root-mean-square difference D between calculated and observed frequencies given by eq 10. Table V also contains for each molecule the values

$$D = \left[\frac{1}{3N - 6}\sum_i^{3N-6}(\nu_i^{\text{obsd}} - \nu_i^{\text{calcd}})^2\right]^{1/2} \qquad (10)$$

of D for the calculated frequencies from the model SVFF and the published force fields, and not surprisingly it may be seen that the more sophisticated force fields generate smaller errors than does the SVFF. Comparison of the errors W and D produced by the model SVFF shows that the entropy-weighted error is consistently smaller than the unweighted error, as would be expected; in contrast, the published force fields often give rise to a larger entropy-weighted error than unweighted error.

Calculations of Thermodynamic Quantities

We have used the model SVFF in conjunction with QREL to calculate the quantities $(G^\ominus - \epsilon)$, $(H - E_0)$, E_{zp}, and $TS^\ominus$, at 298.16 K and standard state (1 atm), for each of the compounds involved in the force field development by assuming ideal gas conditions. These quantities are related by eq 11, and their values are

$$(G^\ominus - \epsilon) = (H - E_0) + E_{\text{zp}} + TS^\ominus \qquad (11)$$

presented in Table VI in units of kcal mol^{-1} along with errors expressed as percentages. It is assumed that the errors arise solely from the vibrational contributions; obviously, this assumption is incorrect as the calculated rotational contributions are also certainly in error since idealized geometries were used. The rotational contributions affect the free energy only via the entropy term, and associated errors could be estimated if the true molecular geom-

---

(37) R. Gaufres and M. Bejaud-Bianchi, *Spectrochim. Acta, Part A*, **27A**, 2249 (1971).

(38) J. R. Durig, C. M. Player, Jr., and J. Bragin, *J. Chem. Phys.*, **54**, 460 (1971).

(39) S. Suzuki, J. L. Bribes, and R. Gaufres, *J. Mol. Spectrosc.*, **47**, 118 (1973).

(40) (a) J. E. Bertie and S. Sunder, *Can. J. Chem.*, **51**, 3344 (1973). (b) When we had completed this part of the work we noted a paper by R. Stølevik [*Acta Chem. Scand., Ser. A*, **31A**, 359 (1977)] in which a similar approach was used. An H···C rather than an H···Me contribution was defined.

Table IV. Torsional Force Constants for Model SVFF

(a) Force Constants for Molecules Used in Force Field Development

molecule	torsional coordinate	force constant, mdyn Å rad^{-2}
ethane	C–C	0.0798
propane	C–C	0.0972
2-methylpropane	C–C	0.1146
2,2-dimethylpropane	C–C	0.1320
butane, anti	CH_2–CH_2	0.1146
	C–CH_3	0.0972
chloroethane	C–C	0.1102
2-chloropropane	C–C	0.1276
2-chloro-2-methylpropane	C–C	0.1450
1-chloropropane, anti	C–CH_2Cl	0.1276
	C–CH_3	0.0798

molecule	torsional coordinate	force constant, mydn Å rad^{-2}
1-chloropropane, gauche	C–CH_2Cl	0.1894
	C–CH_3	0.0936
bromoethane	C–C	0.1122
2-bromopropane	C–C	0.1296
2-bromo-2-methylpropane	C–C	0.1470
1-bromopropane, anti	C–CH_2Br	0.1296
	C–CH_3	0.0652
1-bromopropane, gauche	C–CH_2Br	0.2404
	C–CH_3	0.0802

(b) Torsional Force Constants for Other Molecules

molecule[a]	torsional coordinate	force constant, mdyn Å rad^{-2}	model[b]
cyclohexane, chair	C–C	0.1359	
butane, gauche	CH_2–CH_2	0.1359	cyclohexane
	C–CH_3	0.0972	anti butane
2-methylbutane, C_1	CH–CH_3	0.1146	2-methylpropane
	CH_2–CH	0.1533	
	CH_2–CH_3	0.0972	anti butane
2-chlorobutane, $_{H}S_{H}$	CCl–CH_3	0.1276	2-chloropropane
	CCl–CH_2	0.155	
	CH_2–CH_3	0.0972	anti butane
2-chlorobutane, $_{H}S_{C}$	CCl–CH_3	0.1102	chloroethane
	CCl–CH_2	0.155	
	CH_2–CH_3	0.0972	anti butane
2-chlorobutane, $_{H}S_{H'}$	CCl–CH_3	0.1102	chloroethane
	CCl–CH_2	0.20	
	CH_2–CH_3	0.0972	anti butane
2-bromobutane, $_{H}S_{H}$	CBr–CH_3	0.1296	2-bromopropane
	CBr–CH_2	0.17	
	CH_2–CH_3	0.0972	anti butane
2-bromobutane, $_{H}S_{C}$	CBr–CH_3	0.1122	bromoethane
	CBr–CH_2	0.17	
	CH_2–CH_3	0.0972	anti butane
2-bromobutane, $_{H}S_{H'}$	CBr–CH_3	0.1122	bromoethane
	CBr–CH_2	0.22	
	CH_2–CH_3	0.0972	anti butane
1,2-dichloroethane, anti	C–C	0.164	
1,2-dichloroethane, gauche	C–C	0.33	

molecule[a]	torsional coordinate	force constant, mdyn Å rad^{-2}	model[b]
1,2-dibromoethane, anti	C–C	0.225	
1,2-dibromoethane, gauche	C–C	0.60	
pentane, anti, anti	CH_2–CH_2	0.1146	anti butane
	CH_2–CH_3	0.0972	anti butane
1-chloro-2-methylpropane, C_s	C–CH_2Cl	0.145	predicted from anti contributions
	C–CH_3	0.100	
1-chloro-2-methylpropane, C_1	C–CH_2Cl	0.145	
	$C(CH_3)$–CH_3	0.100	
	$C(CH_2Cl)$–CH_3	0.100	
1-bromo-2-methylpropane, C_s	C–CH_2Br	0.147	predicted from anti contributions
	C–CH_3	0.100	
1-bromo-2-methylpropane, C_1	C–CH_2Br	0.147	
	$C(CH_3)$–CH_3	0.100	
	$C(CH_2Br)$–CH_3	0.100	
1-chloro-2,2-dimethylpropane	C–CH_2Cl	0.1624	predicted from anti contributions
	C–CH_3	0.100	
1-bromo-2,2-dimethylpropane	C–CH_2Br	0.1644	predicted from anti contribution
	$C(CH_2Br)\overset{\text{anti}}{\text{———}}CH_3$	0.100	predicted from gauche contributions
	$C(CH_2Br)\overset{\text{gauche}}{\text{———}}CH_3$	0.100	

[a] Notation for secondary alkyl halides: subscripts denote the atoms antiperiplanar to the halogen across the two adjacent C–C bonds. cf.: W. H. Moore and S. Krimm, *Spectrochim. Acta, Part A*, 29A, 2025 (1973); C. G. Opaskar and S. Krimm, *ibid.*, 23A, 2261 (1967). The same notation is used in Table VIII. [b] Force constant assumed equal to that for corresponding coordinate in model compound.

etries were known. However, since our interest is not chiefly in this contribution, we have chosen to neglect it as a source of error. The errors in the vibrational contributions were estimated by comparison with the values calculated on the basis of the observed frequencies specified above.

Inspection of Table VI reveals that the largest contribution to ($G^\ominus - \epsilon$) arises from the zero-point energy E_{zp}, which has values from 20 up to 100 kcal mol^{-1} over the range of molecules considered; the error in calculated E_{zp} is less than 2% for all molecules, and in most cases is less than 1%. The acceptably small errors in zero-point energies are especially satisfactory since the program was specifically tailored, as noted above, to reproduce low frequencies, which we expect to have the major significance in the most important projected applications (solvation studies, enzyme models). Zero-point energies are of course determined mainly by higher frequencies, the absolute magnitude for any molecule being directly proportional to the sum of all frequencies. The other NPE contribution to the enthalpy is the ($H - E_0$) term (mainly thermal energy). This term has only a modest value, between 2 and 5 kcal mol^{-1} for these molecules, and can be related linearly to the number of modes that each molecule has; again, the calculated errors in ($H - E_0$) are all less than 2% and in most cases less than 1%. The temperature–entropy term $TS^\ominus$ has values from 13 to 24 kcal mol^{-1} for these molecules under the stated conditions; in all cases the calculated error is less than 1%. The value of ($G^\ominus - \epsilon$) is obtained by subtracting $TS^\ominus$ from ($H - \epsilon$), which is the sum of ($H - E_0$) and E_{zp}; as each of these contributions is individually positive, the effect of the subtraction is to make ($G^\ominus - \epsilon$) less positive. Hence ($G^\ominus - \epsilon$) has values ranging from 7 to 80 kcal mol^{-1}, and the calculated error is less than 2% in all cases but one. The low errors associated with these calculated values in Table VI clearly demonstrate the applicability of the model SVFF for calculation of the vibrational contributions to ($G^\ominus - \epsilon$).

Frequency Calculations for Other Molecules

In order to extend the range of applicability of the model SVFF, we performed calculations for a number of molecules which were

Table V. Comparison of Results from Model SVFF and Published Force Fields (PFF) in Calculations of Frequencies

molecule[a]	error in vibrational entropy[b] *P*, %		rms weighted error[b] *W*, cm^{-1}		rms difference *D*, cm^{-1}	
	SVFF	PFF	SVFF	PFF	SVFF	PFF
methane[c]	−3.84	−0.67	20.1	1.91	35.9	1.18
ethane[d]	−0.34	−2.88	12.6	9.81	74.0	18.5
propane[d]	−1.68	−8.23	15.0	31.5	54.8	22.6
2-methylpropane[e]	0.06	−10.4	15.4	38.1	40.6	15.6
2,2-dimethylpropane[e]	−0.92	−15.9	24.3	52.1	40.3	23.1
butane, anti[d]	−4.65	−15.8	19.8	42.2	49.9	14.8
chloromethane[f]	0.29	0.54	10.1	2.15	56.2	14.4
chloroethane[g]	−0.91	−10.5	2.81	35.8	28.6	16.3
2-chloropropane[h]	−1.87	0.07	17.2	5.73	37.3	9.95
2-chloro-2-methylpropane[i]	−0.23	22.1	28.8	137.2	41.2	57.9
1-chloropropane, anti[g]	−0.38	−6.16	2.09	19.9	38.4	24.9
1-chloropropane, gauche[g]	−0.25	−12.8	2.87	34.1	35.4	15.8
bromomethane[j]	0.46	1.26	6.87	6.66	63.4	13.9
bromoethane[k]	−0.33	−0.64	2.33	5.20	36.2	5.56
2-bromopropane[l]	0.87	−10.2	16.0	43.2	39.1	24.7
2-bromo-2-methylpropane[m]	4.17	−0.35	36.8	30.6	46.9	13.8
1-bromopropane, anti[n]	0.06	−1.48	2.16	13.1	40.5	8.42
1-bromopropane, gauche[n]	−0.09	−8.68	2.07	26.1	39.3	9.83

[a] Superscripts refer to source of published force field. [b] All entropies (and entropy-weighted errors) calculated for 298.16 K. [c] L. H. Jones and R. S. McDowell, *J. Mol. Spectrosc.*, 3, 632 (1959). [d] Reference 9. [e] Reference 17. [f] W. T. King, I. M. Mills, and B. C. Crawford, *J. Chem. Phys.*, 27, 455 (1957). [g] R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, 30, 290 (1969). [h] W. H. Moore and S. Krimm, *Spectrochim. Acta, Part A*, 29A, 2025 (1973). (Only the 20 modes with frequencies below 2000 cm^{-1} are included.) [i] Reference 31. [j] Reference 33. [k] Reference 36. [l] R. G. Snyder, *J. Mol. Spectrosc.*, 28, 273 (1968). [m] Reference 37. [n] Reference 32.

Table VI. Contributions to $(G^{\ominus} - \epsilon)$ Calculated by Using Model SVFF

molecule	$(G^{\ominus} - \epsilon)$,[a,b] kcal mol^{-1}		$(H - E_0)$, kcal mol^{-1}		E_{zp}, kcal mol^{-1}		$TS^{\ominus}$,[b] kcal mol^{-1}	
	calcd	% error	calcd	% error	calcd	% error	calcd	% error[c]
methane	15.99	1.40	2.40	−0.04	26.86	0.83	13.27	−0.01
ethane	31.37	1.46	2.80	−0.11	44.83	1.02	16.26	−0.01
propane	46.35	1.86	3.47	−0.61	62.04	1.37	19.16	−0.15
2-methylpropane	62.95	0.23	4.19	−0.19	79.59	0.20	20.84	0.01
2,2-dimethylpropane	79.58	0.34	4.95	−0.69	96.31	0.28	21.68	−0.17
butane, anti	78.60	0.53	4.20	−1.19	79.57	0.42	21.29	−0.61
chloromethane	8.62	1.76	2.49	−0.02	22.82	0.67	16.68	0.00
chloroethane	23.71	0.75	3.14	−0.38	40.16	0.44	19.59	−0.05
2-chloropropane	39.56	0.99	3.91	−0.66	57.20	0.65	21.55	−0.20
2-chloro-2-methylpropane	56.07	1.01	4.70	−0.30	73.93	0.78	22.55	−0.04
1-chloropropane, anti	39.55	−0.30	3.98	−0.23	57.46	−0.21	21.88	−0.05
1-chloropropane, gauche	39.70	−0.17	3.91	−1.87	57.54	−0.12	21.75	−0.33
bromomethane	7.33	4.75	2.58	0.03	22.30	1.56	17.51	0.01
bromoethane	22.35	1.38	3.22	−0.12	39.56	0.78	20.43	−0.02
2-bromopropane	38.49	0.61	4.00	0.30	56.83	0.43	22.34	0.10
2-bromo-2-methylpropane	55.24	0.71	4.78	1.47	73.76	0.66	23.30	0.70
1-bromopropane, anti	38.16	−0.37	4.09	−0.01	56.81	−0.25	22.74	0.01
1-bromopropane, gauche	38.37	−0.12	4.00	−0.13	56.93	−0.08	22.56	−0.01

[a] $(G^{\ominus} - \epsilon) = (H - E_0) + E_{zp} - TS$. [b] Standard state at 1 atm and 298.16 K. [c] Error in entropy assumed to arise solely from vibrational contribution (see text).

not among those used in its development. The structural parameters and force constants for stretching and bending given in Tables I–III were used, and the torsional force constants used for these molecules are given in Table IVb. Application of the values of bending force constants, contained in Table III, required the formulation of simple rules to resolve certain ambiguities: some bending coordinates in these additional molecules are substituted both at apical and terminal atoms or are substituted both in anti and gauche fashions at a terminal atom, whereas only a single type of substitution occurs in each of the molecules used in the force field development. We adopted the following conventions for deciding which type of substitution determines the force constant value for any particular bending coordinate: terminal substitution takes precedence over apical substitution and anti substitution takes precedence over gauche substitution.

The agreement of calculated and observed frequencies was generally good although there were some large discrepancies for particular modes; for instance, calculated bending and stretching modes involving the halogen atoms of the 1,2-dihaloethanes are considerably in error. As suggested above, these failings probably reflect the inability of the SVFF to account properly for strongly coupled vibrational modes. Alternatively, it may be argued in this case, and in other cases such as those in which the type of substitution about a bending coordinate is not unambiguously designated, that the coordinates should be recognized as occurring in different local environments and that therefore different force constant values should be assigned to them.

Table VII contains values of the errors *P*, *W*, and *D* computed for the low-frequency modes calculated for some of these molecules where observed frequencies are available. It may be seen that the magnitudes of these errors are comparable with those presented in Table V for the molecules used in the force field development, thus satisfactorily demonstrating the application of the model SVFF to these additional molecules.

Further examples, dealing with conformational inversion in cyclohexane derivatives, will be discussed in a future paper.

Rationalization of Force Constants and Discussion of Frequencies for Torsional Modes

Conformational analysis of organic molecules is often discussed in terms of interactions between substituent groups, e.g., repulsions between gauche-related vicinal substituents. An extension of such

Table VII. Errors in Frequencies Calculated for Molecules not Used in Force Field Development

molecule	error in vibrational entropy[a] P, %	rms weighted error in frequencies[a] W, cm^{-1}	rms difference in frequencies D, cm^{-1}
cyclohexane	−1.72	7.76	53.6
1,2-dichloroethane, anti conformer	−7.58	24.5	64.0
1,2-dichloroethane, gauche conformer	−0.39	13.9	44.7
1,2-dibromoethane,[b] anti conformer	−2.89	15.2	52.9
1,2-dibromoethane,[b] gauche conformer	−0.58	30.5	37.1
2-chlorobutane,[c]			
${}_{\mathrm{H}}S_{\mathrm{H}}$ conformer	1.66	11.7	45.0
${}_{\mathrm{H}}S_{\mathrm{C}}$ conformer	0.78	8.60	42.2
${}_{\mathrm{H}}S_{\mathrm{H}'}$ conformer	−0.50	7.61	39.7
2-bromobutane,[c]			
${}_{\mathrm{H}}S_{\mathrm{H}}$ conformer	2.24	15.5	41.9
${}_{\mathrm{H}}S_{\mathrm{C}}$ conformer	0.63	9.55	42.1
${}_{\mathrm{H}}S_{\mathrm{H}'}$ conformer	0.42	8.08	41.7
1-chloro-2-methylpropane,[d]			
C_s conformer	−2.38	20.7	20.0
C_1 conformer	0.31	20.7	21.3
1-bromo-2-methylpropane,[d]			
C_s conformer	−5.39	29.9	25.5
C_1 conformer	−1.77	24.0	18.0

[a] Entropies are calculated for 298.16 K. Errors P and W are estimated on the basis of all the modes; when there is no available observed frequency for a particular mode, its entropy is assumed equal to that computed from the corresponding calculated frequency and there is no resulting contribution to P or W. [b] Error D computed for 14 observed frequencies below 2000 cm^{-1}. [c] Error D computed for 27 observed frequencies below 2000 cm^{-1}. [d] Error D computed for 13 observed frequencies below 1000 cm^{-1}.

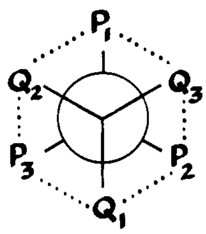


Figure 1. Newman projection of an ethane-like torsional coordinate showing the six vicinal interactions between gauche-related substituents.

Table VIII. Torsional Force Constant Contributions (F) from Vicinal Interactions between Gauche-Related Substituents for Symmetric Torsional Oscillators

gauche interactn	F, mdyn Å rad^{-2}	gauche interactn	F, mdyn Å rad^{-2}
H···H	0.0133	H···CH_2Me	0.022
H···Me	0.022	H···CH_2Cl	0.0133
H···Cl	0.0285	H···CH_2Br	0.006
H···Br	0.0295		

ideas suggests that restrictions to torsional motion, and hence values of torsional force constants, might also be governed by the nature of interactions between gauche-related substituents. We analyzed the torsional coordinates of the molecules used in the force field development by means of Newman projections and established a scheme whereby the value of a torsional force constant might be found as the sum of six contributions determined by the six vicinal interactions between gauche-related substituents. These additive "gauche contributions" (symbolized by $R_1 \cdots R_2$) were considered to be transferable between molecules: the value of the contribution H···H was determined from the ethane torsional force constant and application of this value to other methyl- and halogen-substituted ethanes enabled the contributions H···Me and H···X to be determined.[40b] These values of gauche contributions were used successfully to predict force constants for torsional modes of the methyl- and halogen-substituted propanes. Thus the frequencies of the skeletal torsional modes of the anti conformers of 1-chloropropane and 1-bromopropane were calculated to be 121 and 114 cm^{-1}, respectively, in excellent agreement with the corresponding observed gas-phase frequencies[11a] at 121 and 115 cm^{-1}. This additive scheme was found to work well for all the molecules used in the force field development which could be seen by inspection to possess symmetric torsional potentials,[41] such that small displacements in torsional coordinates resulted in the same changes in gauche interactions irrespective of the directions of the displacements. For these molecules, therefore, any torsional force constant Y may be expressed as a sum of six gauche contributions $P_i \cdots Q_j$ illustrated by Figure 1, whose values are given in Table VIII. The torsional force constants appearing in Table IVa for these molecules were obtained from Table VIII by means of eq 12.

$$Y = \sum_i^3 \sum_j^3 P_i \cdots Q_j \quad (i \neq j) \tag{12}$$

Molecules containing two or more equivalent methyl groups have vibrational modes which are symmetric and asymmetric combinations of the methyl group torsional motions. The observed frequencies for these modes are often split by an appreciable frequency difference whereas the corresponding calculated frequencies are similar. Some of the observed splitting may arise from intermolecular interactions in condensed phases,[25] but much may be due to genuine intramolecular effects. The torsional frequencies calculated for the 2-halopropanes from the gauche contributions in Table VIII agree well with the observed maxima of the gas-phase absorption bands for the torsional modes.[42] In general it would seem that average torsional frequencies are higher in condensed phases than in the gas phase,[11,43,44] and it is of interest to note the way in which these frequency shifts accompanying phase changes might affect the torsional frequencies of the anti conformers of 1,2-disubstituted ethanes. The observed torsional frequency of solid 1,2-dichloroethane is 34 or 42 cm^{-1} higher than that observed in the gas phase for the anti conformer.[45a,b] The solid-phase torsional frequency[30] for anti butane is 155 cm^{-1} and the value[45a] for the bulk liquid is 130 cm^{-1}, but the gas-phase value is unknown; if the frequency shift accompanying vaporization is of the same order for anti butane as for *anti*-1,2-dichloroethane then the gas-phase value might agree with the frequency of 125 cm^{-1} calculated on the basis of the gauche contributions to the torsional force constant from Table VIII. However, the torsional frequencies for both *anti*-1,2-dichloroethane and *anti*-1,2-dibromoethane calculated on the basis of torsional force constants obtained from these tabulated contributions were found to be too low, at 114 and 97 cm^{-1}, respectively, which may point to the inadequacy of the proposed force constant additivity scheme for symmetric torsional oscillators such as these. An alternative rationalization based on contributions specified by pairs of antiperiplanar vicinal substituents was investigated: this scheme allowed for satisfactory treatment of the torsional force constants

---

(41) Symmetric torsional potentials in this sense include (see Figure 1) both those where $P_2 = P_3$ and $Q_2 = Q_3$ and those where $P_1 = P_2 = P_3$ but $Q_1 \neq Q_2 \neq Q_3$.

(42) K. D. Möller, A. R. DeMeo, D. R. Smith, and L. H. London, *J. Chem. Phys.*, **47**, 2609 (1967).

(43) E.g.: Average observed torsional frequencies in gas,[42] liquid,[33] and solid[44] phases are 259, 265, and 266 cm^{-1}, respectively, for 2-chloropropane and 256, 258, and 264 cm^{-1}, respectively, for 2-bromopropane.

(44) J. R. During, C. M. Player, Jr., Y. S. Li, J. Bragin, and C. W. Hawley, *J. Chem. Phys.*, **57**, 4544 (1972).

(45) (a) J. R. During, K. K. Lau, S. E. Hannum, and F. G. Baglin, *J. Mol. Struct.*, **9**, 291 (1971); (b) S. Mizushima, T. Shimanouchi, I. Harada, Y. Abe, and H. Takeuchi, *Can. J. Phys.*, **53**, 2085 (1975). (c) Cited by: H. Taub, H. R. Danner, H. L. McMurry, and R. M. Bruger, *Surf. Sci.*, **76**, 50 (1978).

Table IX. Comparison of Calculated with Experimental Molar Entropies. Treatment of Torsional Motions in Calculations of Thermodynamic Functions

molecule	temp, K	calcd molar entropy,[a] cal deg^{-1} mol^{-1}: free internal rotatns[c]	calcd molar entropy,[a] cal deg^{-1} mol^{-1}: harmonic torsional vibratns[d]	exptl molar entropy,[b] cal deg^{-1} mol^{-1}
ethane	184.1	51.42	49.36	49.54 ± 0.15[h]
propane	231.04	63.96	60.29	60.45 ± 0.10[i]
2-methylpropane	261.44	72.84	67.08	67.52 ± 0.10[j]
2,2-dimethylpropane	282.61	79.22	71.22	71.71 ± 0.3[k]
butane[e]	272.66	77.86	70.68	72.05 ± 0.2[l]
chloroethane	285.36	67.08	65.36	65.31 ± 0.10[m]
1,2-dichloroethane[f]	356.8	80.40	76.51	77.10 ± 0.15[n]
1,2-dibromoethane[g]	404.9	88.22	84.29	85.98 ± 0.15[n]

[a] Calculated entropies refer to ideal gases at standard state 1 atm. [b] Experimental entropies from heat capacity measurements, with corrections for gas imperfection. [c] Calculated by the method of J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, 17, 1064 (1949). [d] Calculated using torsional force constants from Table IV. [e] Mole fractions of 0.74 for anti and 0.26 for gauche conformers estimated at the boiling point from the enthalpy difference[29] obtained from temperature variation of relative intensities of infrared absorptions and calculated entropy difference. [f] Mole fractions of 0.74 for anti and 0.26 for gauche conformers estimated by interpolation of data obtained from electron diffraction experiments of K. Kveseth, *Acta Chem. Scand., Ser. A*, 28A, 482 (1974). [g] Mole fractions of 0.82 for anti and 0.18 for gauche conformers estimated from the electron diffraction result of A. Almenningen, O. Bastiansen, A. Haaland, and H. M. Seip, *Angew. Chem., Int. Ed. Engl.*, 4, 819 (1965), assuming free energy difference to be temperature independent. [h] R. K. Witt and J. D. Kemp, *J. Am. Chem. Soc.*, 59, 273 (1937). [i] J. D. Kemp and C. J. Egan, *ibid.*, 60, 1521 (1938). [j] J. G. Aston, R. M. Kennedy, and S. C. Schumann, *ibid.*, 62, 2059 (1940). [k] J. G. Aston and G. H. Messerley, *ibid.*, 58, 2354 (1936). [l] *ibid.*, 62, 1917 (1940). [m] J. Gordon and W. F. Giauque, *ibid.*, 70, 1506 (1948). [n] W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, 16, 303 (1948).

Table X. Calculated Molar Entropies for Alkanes, Chloroalkanes, and Bromoalkanes

molecule	molar entropy,[a] cal deg^{-1} mol^{-1}: this work	molar entropy,[a] cal deg^{-1} mol^{-1}: lit.[b]
cyclohexane	71.07	71.28
2-methylbutane[c]	80.03	82.12
1-chloropropane[d]	74.38	76.27
2-chloropropane	72.28	72.70
1-chloro-2-methylpropane[e]	81.19	84.56
2-chloro-2-methylpropane	75.63	77.00
2-chlorobutane[f]	81.52	85.94
1-chloro-2,2-dimethylpropane	82.49	
bromoethane	68.50	68.71
1-bromopropane[g]	77.20	79.08
2-bromopropane	74.93	75.53
1-bromo-2-methylpropane[h]	83.95	
2-bromo-2-methylpropane	78.14	79.34
	86.82[i]	86.6[i,j]
2-bromobutane[k]	83.83	88.50
1-bromo-2,2-dimethylpropane	88.46	
	105.48[l]	105.3[l,j]

[a] Entropies at 298.16 K, standard state 1 atm, unless otherwise indicated. [b] D. R. Stull, E. F. Westrum, Jr., and G. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969. [c] Mole fractions of 0.88 for C_1 and 0.12 for C_s conformers estimated from the enthalpy difference[29] obtained from temperature variation of relative intensities of infrared absorptions and calculated entropy difference. [d] Mole fractions of 0.65 for gauche and 0.35 for anti conformers estimated from the enthalpy difference obtained from temperature variation of relative intensities of infrared absorptions (C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *Bull. Chem. Soc. Jpn.*, 28, 330 (1955)) and calculated entropy difference. [e] Mole fractions of 0.59 for C_1 and 0.41 for C_s conformers estimated from the enthalpy difference obtained from temperature variation of relative intensities of infrared absorptions (E. Wyn-Jones and W. J. Orville-Thomas, *Trans. Faraday Soc.*, 64, 2907 (1968)) and calculated entropy difference. [f] Mole fractions of 0.58 for ${}_{\mathrm{H}}S_{\mathrm{H}}$, 0.25 for ${}_{\mathrm{H}}S_{\mathrm{C}}$, and 0.17 for ${}_{\mathrm{H}}S_{\mathrm{H}'}$ (A. I. Karelin, Yu. A. Pentin, and O. D. Ul'yanova, *Russ. J. Phys. Chem. (Engl. Transl.)*, 41, 1450 (1967)). [g] Mole fractions of 0.63 for gauche and 0.37 for anti conformers estimated from spectroscopic observations (C. Komaki et al., *Bull. Chem. Soc. Jpn.*, 28, 330 (1955)) and calculated entropy difference. [h] Mole fractions of 0.53 for C_1 and 0.47 for C_s conformers estimated from spectroscopic observations (E. Wyn-Jones and W. J. Orville-Thomas, *Trans. Faraday Soc.*, 64, 2907 (1968)) and calculated entropy difference. [i] At 400 K. [j] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 28, 301 (1958). [k] Mole fractions of 0.67 for ${}_{\mathrm{H}}S_{\mathrm{H}}$, 0.18 for ${}_{\mathrm{H}}S_{\mathrm{C}}$, and 0.15 for ${}_{\mathrm{H}}S_{\mathrm{H}'}$ (A. I. Karelin et al., *Russ. J. Phys. Chem. (Engl. Transl.)*, 41, 1450 (1967)). [l] At 470 K.

for the *anti*-1,2-dihaloethanes but in consequence involved a greater number of parameters than did the original scheme. However, we did choose to use this alternative scheme for predictions of some of the force constant values presented in Table IVb.

Torsional Motions: Vibrations or Internal Rotations?

In the work described above we have consistently regarded torsional motions as harmonic vibrations, but the manner in which such motions ought properly to be treated depends upon the nature of the associated potential energy changes. Two extreme cases may be considered: first, when the motion occurs within a truly harmonic potential and, second, when there is no potential energy change associated with the motion, which is therefore a free internal rotation. In the former case the motion is properly regarded as a harmonic oscillation; its frequency may be obtained from a normal-coordinate calculation, and hence its contribution to the total vibrational partition function may be evaluated by using eq 5. If the motion is truly a free internal rotation, then its partition function may be estimated from a knowledge of the reduced moment of inertia of the molecule about the internal rotational axis. The torsional motions of most molecules have characters intermediate between these two extremes and are often described as hindered internal rotations. Calculation of partition functions for hindered internal rotational motions is usually achieved[46] by prior calculation of the partition function for a free internal rotational motion and subsequent reduction of the value by an amount determined by the known or assumed height of the hindering energy barrier. The requirement for knowledge of the barrier height makes this method for the calculation of partition functions and thence entropies rather unsatisfactory; indeed, many barrier heights are themselves estimated from experimental entropy determinations.

A torsional potential is often well represented by a cosine function with an amplitude η equal to the barrier height. If $\eta \ll RT$, then the motion may be approximated as free internal rotation, and if $\eta \gg RT$, then the valid approximation is that of the harmonic oscillator. The problem remains that often $\eta \approx RT$; nevertheless, as noted above, we have chosen to treat all torsional motions as harmonic vibrations. The validity of this approximation may be tested by calculating the molar entropies of a number of significant compounds by treating their torsional motions first as free internal rotations and second as harmonic torsional vibrations; these treatments might be expected to overestimate and to underestimate respectively the entropies of the compounds. The two calculated values of entropy may then be compared with the experimental value of the third-law entropy for each molecule in order to decide which calculation gives better agreement with the experiment. Results are presented in Table IX.

These results provide a true comparison of calculated with experimental values of thermodynamic functions, because the

---

(46) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 10, 428 (1942).

entropies calculated[47] by using the model force field are compared with entropies determined from measurements of the temperature coefficients of heat capacities. Several of the molecules considered here exhibit rotational isomerism and occur as mixtures of rotamers in the gas phase. The calculated molar entropies include contributions from entropies of mixing on the basis of estimations of the proportions of rotamers present, obtained either from electron diffraction experiments or from spectroscopic determinations of enthalpy differences together with calculated values of entropy differences.

It may be seen from Table IX that better agreement with the experimental value for the molar entropy is consistently provided for the molecules studied by the result calculated on the basis of harmonic torsional vibrations, which is either equal to or slightly less than the experimental value. By contrast, the result calculated on the basis of free internal rotation is always appreciably greater than the experimental value. This successful treatment of torsions as harmonic vibrations provides support for the procedure adopted throughout our work on NPE effects and suggests that these motions may often be better described as loose vibrations than as hindered rotations.

Further Calculations of Molar Entropies

Whereas Table IX contains experimental entropies which are true empirical results, many published molar entropies are semiempirical values obtained by application of statistical thermodynamic expressions to observed calculated structural and spectroscopic data, and the accuracy of these entropies depends upon the quality of the data used and the validity of any assumptions involved such as the use of the harmonic approximation. Using the SVFF, we have calculated molar entropies for a number of molecules for which noncalorimetric estimations are for the most part available in the literature. Comparisons show reasonable agreement, as seen in Table X.

Acknowledgment. We thank the S.R.C. for support.

---

[47] Details of these calculations are described in: Williams, I. H. Ph.D. thesis, University of Sheffield, 1978.

Calculations of Kinetic Isotope Effects for S_N2 Bromine Exchange Reactions of Alkyl Bromides: Development of Transition-State Force Field for Calculation of NPE Effects

James McKenna,* Leslie B. Sims, and Ian H. Williams

Contribution from the Department of Chemistry, The University, Sheffield S3 7HF, England.
Received December 6, 1979

Abstract: A transition-state force field for S_N2 bromine-exchange reactions with a series of alkyl bromides has been developed and checked by calculation of ^{14}C primary and (mostly) ^2H secondary hydrogen isotope effects for these reactions in reasonable agreement with experimental values for related reactions.

Introduction

In the preceding paper[1] we outlined proposals for investigation of the role of factors other than potential energy in chemical reactivity. We felt that a range of the Finkelstein exchanges[2]

$$X^- + RX \rightarrow RX + X^-$$

would provide a useful area in which to gain preliminary experience in application of our procedure for calculating NPE effects, and we chose to study bromine exchanges; other theoretical studies[3,4] on such substitution reactions have been made in recent years. Suitable force fields for the reactant organic bromides have been described in the preceding paper,[1] and the next essential requirement was for force fields for the exchange transition states. In this paper we describe the selection of appropriate transition-state force fields, based on Ingold's earlier work[2] and calibrated by calculation of kinetic isotope effects for the Finkelstein reactions and comparison of these calculated values with experimental values for related reactions. Relative NPE effects for the exchange reactions of different alkyl halides are then described in the following paper.[5]

In principle, optimized geometries of all molecular species could be obtained by energy minimization procedures based either on an empirical force field or on quantum mechanical calculations and vibrational frequencies then obtained as the eigenvalues of a potential energy matrix constructed in an appropriate coordinate system. However, for simplicity we adopted a "somewhat approximate analysis" (following Ingold)[2,6] based on idealized geometries and a model simple valence force field (SVFF).[7] Such a field is known already[8] to provide an adequate basis for calculation of kinetic isotope effects.

Models for Reactants and Transition States

Reactants. The range of reactants studied is indicated in the tables. The model SVFF described previously[1] was applied to all of these, with idealized geometries being assumed, in which all interbond angles took the tetrahedral value 109.47122° [$\cos^{-1}(-^1/_3)$] and bond lengths were 1.10 Å for C–H, 1.53 Å for C–C, and 1.95 Å for C–Br. Atomic weights on the unified mass scale were employed,[9] and the isotope ^{79}Br was used for all bromine atoms. All substituents about C–C bonds were assumed to be

---

[1] C. D. Chalk, B. G. Hutley, J. McKenna, L. B. Sims, and I. H. Williams, preceding paper.

[2] C. K. Ingold, *Q. Rev., Chem. Soc.*, **11**, 1 (1957).

[3] (a) M. H. Abraham, P. L. Grellier, and M. J. Hogarth, *J. Chem. Soc., Perkin Trans. 2*, 1365 (1975); (b) D. F. DeTar, D. F. McMullen, and N. P. Luthra, *J. Am. Chem. Soc.*, **100**, 2484 (1978).

[4] H. B. Schlegel, K. Mislow, F. Bernardi, and A. Bottoni, *Theor. Chim. Acta*, **44**, 245 (1977) and literature cited therein.

[5] C. D. Chalk, J. McKenna, L. B. Sims, and I. H. Williams, following paper in this issue.

[6] P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *J. Chem. Soc.*, 3200 (1955).

[7] All calculations in this series of papers have been performed on an ICL 1906 S computer by using a program QREL′ which calculates contributions to $(G - \epsilon)^{\ominus}$ for individual molecular species and hence isotope effects.

[8] G. W. Burton, L. B. Sims, J. C. Wilson, and A. Fry, *J. Am. Chem. Soc.*, **99**, 3371 (1977); cf ref 20.

[9] In our previous work atomic weights on the physical mass scale were employed; the effect of changing to the unified mass scale is negligible.