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.

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(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

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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

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(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.

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Table I. Force Constants for Alkyl Bromides[a]

alkyl group	force constants[b]
methyl (Me)	C-Br, 2.93; C-H, 4.85; HCBr, 0.638; HCH, 0.485
ethyl (Et)	C-Br, 2.01; C-C, 5.0; C_α-H, 4.85; C_β-H, 4.7; CCBr, 1.19; HCBr, 0.70; $HC_\alpha C$, 0.58; $HC_\beta C$, 0.635; $HC_\alpha H$, 0.34; $HC_\beta H$, 0.485; τ, 0.1122
isopropyl (*i*-Pr)	C-Br, 2.2; C-C, 5.0; C_α-H, 4.85; C_β-H, 4.7; CCBr, 1.10; CCC, 1.10; HCBr, 0.70; $HC_\alpha C$, 0.58; $HC_\beta C$, 0.635; HCH, 0.485; τ 0.1296
tert-butyl (*t*-Bu)	C-Br, 2.1; C-C, 5.0; C-H, 4.7; CCBr, 1.17; CCC, 1.17; HCC, 0.635; HCH, 0.485; τ, 0.147
n-propyl[c] (*n*-Pr)	C-Br, 2.18; C-C, 5.0; C_α-H, 4.85; $C_{\beta,\gamma}$-H, 4.7; CCBr, 0.99; CCC, 1.27; HCBr, 0.70; $HC_\alpha C$, 0.58; $HC_\beta C$, 0.61; $HC_\gamma C$, 0.635; $HC_\alpha H$, 0.34; $HC_\beta H$, 0.47; $HC_\gamma H$, 0.485; $\tau(C_\alpha\text{-}C_\beta)$, 0.1296; $\tau(C_\beta\text{-}C_\gamma)$, 0.0652
isobutyl[c] (*i*-Bu)	C-Br, 1.67; C-C, 5.0; C_α-H, 4.85; $C_{\beta,\gamma}$-H, 4.7; CCBr, 1.19; $C_\alpha C_\beta C_\gamma$, 1.20; $C_\gamma C_\beta C_\gamma$, 0.96; HCBr, 0.70; $HC_\alpha C$, 0.58; $HC_\beta C$, 0.68; $HC_\gamma C$, 0.635; $HC_\alpha H$, 0.34; $HC_\gamma H$, 0.485; $\tau(C_\alpha\text{-}C_\beta)$, 0.147; $\tau(C_\beta\text{-}C_\gamma)$, 0.100
neopentyl (neo-Pe)	C-Br, 2.18; C-C, 5.0; C_α-H, 4.85; C_γ-H, 4.7, CCBr, 1.19; $C_\alpha C_\beta C_\gamma$ (anti to Br), 1.27; $C_\alpha C_\beta C_\gamma$ (gauche to Br), 1.20; $C_\gamma C_\beta C_\gamma$, 1.03; HCBr, 0.70; $HC_\alpha C$, 0.58; $HC_\gamma C$, 0.635, $HC_\alpha H$, 0.34; $HC_\gamma H$, 0.485; $\tau(C_\alpha\text{-}C_\beta)$, 0.1644; $\tau(C_\beta\text{-}C_\gamma)$, 0.100

[a] From preceding paper. [b] Diagonal force constants (elements of SVFF) assigned to coordinates as specified, with units of mdyn $Å^{-1}$ for stretching and mdyn Å rad^{-2} for bending (including torsional, τ) coordinates. [c] Conformer with C_s symmetry.

Table II. Nature of Substituents in Transition States (see Figure 1)

	substituents				
alkyl group	P	P′	Q	R	R′
Me	H	H	H		
Et	H	H′	C	H	H
i-Pr	Me	Me	H		
t-Bu	Me	Me	C	H	H
n-Pr	H	H′	C	H	Me
i-Bu	H	H	C	Me	H
neo-Pe	H	H′	C	Me	Me

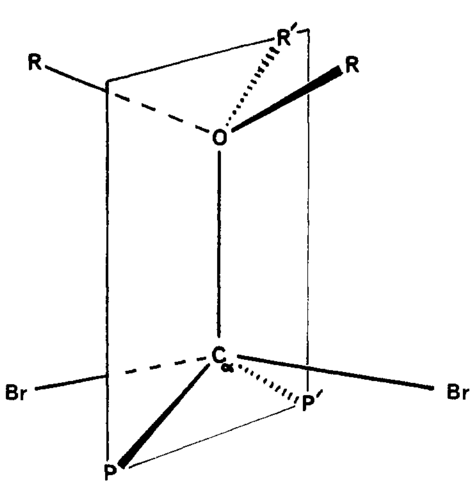

Figure 1. Transition-state configurations and conformations.

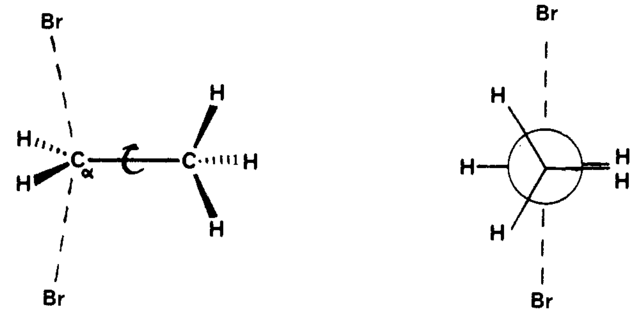

Figure 2. Torsional coordinate in ethyl bromide transition state.

perfectly staggered, and for those molecules having the possibility of rotational isomerism only the conformers with C_s symmetry were considered. The force constants for each molecule are given in Table I.

Transition-State Geometries and Force Constants. For consistency with the assumed reactant geometries and for the sake of simplicity, we adopted the same idealized values for bond lengths and bond angles in the transition states, except for the partial bond lengths and the bond angles involving C_α, for which we used the geometries specified by Ingold's "plastic" model[6] (Tables II and III and Figure 1). In the absence of any detailed knowledge concerning the electronic structure of the transition states, their force constants could all be regarded as variables with values chosen arbitrarily to provide agreement between calculated and observed kinetic isotope effects. Changes in stretching force constants may be related to changes in bond lengths via Badger's rule, and it seems reasonable that bending force constants should vary with changes in interbond angles. Sims[8] has utilized an approximate expression relating any stretching force constant F_{XY} to a change in the order of the bond X-Y

$$F_{XY} = n_{XY}F^{\circ}_{XY} \tag{1}$$

where n_{XY} is the bond order and F°_{XY} is the force constant for a bond order of unity; here bond order is used in a rather intuitive sense as a convenient index, linking bonding changes to force constant changes. Several different rules relating bending force constants to the bond orders of the participating bonds have been proposed by various workers studying isotope effects in different types of reactions: in their study of S_N2 reactions of benzyl chloride Sims and his co-workers[10] set angle bending force constants proportional to the product of the bond orders of the bonds defining the angle, and other workers[11] have made similar assumptions for other S_N2 reactions. Sims' group[8] has also proposed a geometrical factor g_θ as a simple function of the angle θ_{XYZ} between the atoms XYZ defining a bending coordinate:

$$g_\theta = 1.39 + 1.17 \cos \theta_{XYZ} \tag{2}$$

This empirical function was postulated to predict the overall effects of changes in hybridization and nonbonded interactions upon a bending force constant, and it was parametrized[12] so as to enable bending force constants for certain hydrocarbons to be derived from standard values referring to tetrahedral angles and unit bond orders in agreement with values obtained from vibrational analyses. Thus the rule adopted for prediction of transition-state bending force constants in this work is

$$F_{XYZ} = g_\theta(n_{XY}n_{YZ})F^{\circ}_{XYZ} \tag{3}$$

where F°_{XYZ} is the bending force constant for a tetrahedral angle between two bonds each with a bond order of unity. For treatment of torsional coordinates in the S_N2 bromine exchanges we have used a general method of specification for torsional internal coordinates which is correct for torsions of any geometry,[13] adopting the simplification, in the absence of a more rational procedure, that the torsional force constants were in general unchanged between reactants and transition states.

It may be supposed that imposition of an exponential repulsive steric potential onto the harmonic CCBr bending potential of an originally undistorted transition state leads to a new distorted structure in a resultant potential. Consideration of this potential

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(10) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Am. Chem. Soc.*, **94**, 1364 (1972).

(11) (a) A. V. Willi, *Z. Naturforsch., A*, **21A**, 1377, 1385 (1966), *Can. J. Chem.* **44**, 1889 (1966); (b) A. V. Willi and C. M. Won, *J. Am. Chem. Soc.*, **90**, 5999 (1968); *Can. J. Chem.*, **48**, 1452 (1970); (c) J. Bron, *ibid.*, **52**, 903 (1974); (d) W. E. Buddenbaum and V. J. Shiner, Jr., *ibid.*, **54**, 1146 (1976).

(12) L. B. Sims, J. C. Wilson, and E. C. Parton, unpublished results; cf. ref 8.

(13) I. H. Williams, J. McKenna, and L. B. Sims, *J. Mol. Struct.*, **55**, 147 (1979).

Table III. Transition-State Geometries about C_α

alkyl group	bond length[a] C···Br, Å	bond angles,[b] deg					
		C-C_α-H	H-C_α-H (C-C_α-C)*	C-C-Br	H-C-Br	H′-C-Br	Br-C-Br
Me	2.25	120.0	120.0		90.00		180.0
Et	2.26	120.0	120.0	91.47	89.51	89.02	177.0
i-Pr	2.27	120.0	120.0*	91.00	88.00		176.0
t-Bu	2.29		120.0*	90.00			180.0
n-Pr	2.26	120.0	120.0	91.47	89.51	89.02	177.0
i-Bu	2.28	120.0	120.0	92.30	88.85		175.4
neo-Pe	2.30	120.0	120.0	97.19	88.80	84.02	164.6

[a] Values from ref 6. [b] Angles involving bromine atoms calculated from position vectors specified by polar coordinates given in ref 6.

Table IV. Steric Factors S_ω for Transition-State CCBr Bending Force Constants

alkyl group	r, Å	ϕ[a]	ω[a]	S_ω
Et	2.26	11	1.47	1.17
i-Pr	2.27	54.7	1.00	1.20
n-Pr	2.26	11	1.47	1.17
i-Bu	2.28	0	2.30	1.27
neo-Pe	2.30	21	7.19	1.91

[a] Angles in degrees.

Table V. Force Constants for Transition States for S_N2 Bromine Exchange of Alkyl Bromides

alkyl group	force constants[a,b]
Me	C···Br, 1.465; C···Br/C···Br, 1.465; C-H, 4.85; HCBr, 0.443; HCH, 0.390
Et	C···Br, 1.005; C···Br/C···Br, 1.005; C-C, 5.0; C_α-H, 4.85; C_β-H, 4.7; CCBr, 0.948; HCBr, 0.490; H′CBr, 0.494; $HC_\alpha C$, 0.467; $HC_\beta C$, 0.635; $HC_\alpha H$, 0.274; $HC_\beta H$, 0.485; τ, 0.1122
i-Pr	C···Br, 1.10; C···Br/C···Br, 1.10; C-C, 5.405; C_α-H, 4.85; C_β-H, 4.573; CCBr, 0.974; CCC, 1.035; HCBr, 0.501; $HC_\alpha C$, 0.505; $HC_\beta C$, 0.668; HCH, 0.459; τ, 0.1296
t-Bu	C···Br, 0.735; C···Br/C···Br, 0.735; C-C, 5.525; C-H, 4.536; CCBr, 0.629; CCC, 1.150; HCC, 0.677; HCH, 0.452; τ, 0.147
n-Pr	C···Br, 0.936; C···Br/C···Br, 0.936; C-C, 5.0; C_α-H, 4.85; $C_{\beta,\gamma}$-H, 4.7; CCBr, 0.868; CCC, 1.235; HCBr, 0.490; H′CBr, 0.494; $HC_\alpha C$, 0.467; $HC_\beta C$, 0.61; $HC_\gamma C$, 0.635; $H''C_\gamma C$, 0.699; $HC_\alpha H$, 0.274; $HC_\beta H$, 0.47; $HC_\gamma H''$, 0.485; $H''C_\gamma H''$, 0.534; $\tau(C_\alpha-C_\beta)$, 0.2404; $\tau(C_\beta-C_\gamma)$, 0.0802
i-Bu	C···Br, 0.963; C···Br/C···Br, 0.963; C-C, 5.0; C_α-H, 4.85; $C_{\beta,\gamma}$-H, 4.7; CCBr, 0.732; $C_\alpha C_\beta C_\gamma$, 1.235; $C_\gamma C_\beta C_\gamma$, 0.96; HCBr, 0.495; $HC_\alpha C$, 0.467; $HC_\beta C$, 0.68; $HC_\gamma C$, 0.635; $H''C_\gamma C$, 0.699; $HC_\alpha H$, 0.274; $HC_\gamma H''$, 0.485; $H''C_\gamma H''$, 0.534; $\tau(C_\alpha-C_\beta)$, 0.147; $\tau(C_\beta-C_\gamma)$, 0.100
neo-Pe	C···Br, 1.09; C···Br/C···Br, 1.09; C-C, 5.0; C_α-H, 4.85; C_γ-H, 4.7; CCBr, 1.410; $C_\alpha C_\beta C_\gamma$, 1.20; $C_\gamma C_\beta C_\gamma$, 1.03; HCBr, 0.495; H′CBr, 0.529; $HC_\alpha C$, 0.467; $HC_\gamma C$, 0.635; $H''C_\gamma C$, 0.699; $HC_\alpha H$, 0.274; $HC_\gamma H''$, 0.485; $H''C_\gamma H''$, 0.534; $\tau(C_\alpha-C_\beta)$, 0.1644; $\tau(C_\beta-C_\gamma)$, 0.100

[a] Diagonal force constants assigned to coordinates as specified, with units of mdyn $Å^{-1}$ for stretching and mdyn Å rad^{-2} for bending (including torsional τ) coordinates; off-diagonal force constants with units of mdyn $Å^{-1}$ for stretch-stretch interactions. [b] H′ denotes atom making the more acute angle with Br at C_α; H″ denotes atom gauche to C_α.

allowed us to develop a steric factor S_ω, derived in the Appendix as a function of the angular distortion ω of the atoms CCBr from 90°, by which to multiply the value of the bending force constant otherwise obtained from eq 3. Thus the modified bending force constant F'_{CCBr} is given by eq 4 and 5, where r is the C_α···Br bond length, β is the exponent of the repulsive potential, and ϕ is the angle between the plane of the steric pressure and the plane containing the undistorted (90°) CCBr angle. The angular distortions ω are derived from the values of the BrCBr angles given in Table III, which also contains the bond lengths r, and the azimuthal angles ϕ are related to the corresponding polar coordinates for the bromine atoms as given by Ingold.[6] We adopted the same value of the exponent $\beta = 1/0.345 = 2.9$ $Å^{-1}$ as had been used by Ingold and his co-workers[6,14] in determining the transition-state structures which essentially we have employed in this work. Table IV contains the values of ω, r, and ϕ, and the resulting value of S_ω for each transition state. It may be seen that S_ω is of modest value (~1.2) for all cases except neopentyl, for which it is appreciably larger (1.9), in accord with expectations based on Ingold's analysis.[6]

$$F'_{\mathrm{CCBr}} = S_\omega F_{\mathrm{CCBr}} \tag{4}$$

$$S_\omega = 1 + \omega \tan \omega - r\beta\omega(\cos \omega/\cos \phi) \tag{5}$$

The steric forces acting upon the bromine atoms in the transition states must have reactions tending to deform the alkyl groups. The transition states employed undistorted, tetrahedral, geometries for the alkyl groups as for the reactants, but nevertheless the existence of steric interactions between the alkyl groups and the bromine atoms must result in mutual perturbation of the interacting groups; in particular it may be expected that motions of hydrogen atoms close to the bromine atoms are impeded. In recognition of this reciprocal behavior we multiplied bending force constants involving γ-hydrogen atoms proximate to the bromine atoms in the transtion states by a constant factor of 1.1 to represent the increased restriction; thus for each β-methyl substituent the two γ-hydrogen atoms H″ gauche to C_α were affected.

The simplest assumption to make regarding the C···Br partial bond is that each has a bond order of 0.5 in the transition state. Since the relationship between bond energy and bond order is not necessarily linear,[15] this does not necessarily imply that there is no increase in potential energy at the transition-state level, and, moreover, increased steric energies may in any case ensure that the transition state corresponds to an energy maximum with respect to the reaction coordinate. In the *tert*-butyl transition state the angle BrCBr is 180° since the resultant steric pressure of the α-methyl groups on the bromine atoms has no lateral component acting to distort them from collinearity. Ingold[6] described how instead the steric pressure was directed outward and forced the bromine atoms out into a region of gentler energy gradients; thus the C···Br partial bonds are further stretched and weakened, and their stretching force constants are reduced. Consequently for *tert*-butyl we reduced the partial bond order from the value of 0.5, taken by the other transition states, to 0.35; application of eq 1 and 3 then led to diminished values for stretching and bending force constants involving the bromine atoms. The C···Br stretching force constant thus obtained was close to a value estimated graphically from the potential energy contour diagram for the *tert*-butyl transition state given by Ingold.[2,6]

At least for some S_N2 reactions in solution it appears that considerable positive charge is developed at the reaction center.[16] In the transition state for secondary and tertiary alkyl bromides

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(14) I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

(15) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, 1966, pp 81–82.

(16) V. J. Shiner, Jr., *ACS Monogr.*, **No. 167**, 90–159 (1970).

Table VI. Secondary Deuterium Kinetic Isotope Effects k(H)/k(Dx) for Reactions of Alkyl Bromides[a]

alkyl group, type of isotope substn	temp, °C	obsd isotope effect for hydrolysis	calcd isotope effect for S_N2 bromine exchange	contributns to calcd isotope effect		
				MMI	EXC	ZPE
Me, α-d_3	80	0.9[b]	0.998	1.271	0.921	0.852
Et, α-d_2	80	0.983[c]	0.955	1.161	0.937	0.878
i-Pr, α-d	60	1.069[c]	0.960	1.029	0.991	0.942
n-Pr, α-d_2	80	0.980[c,d]	0.941	1.121	0.965	0.870
Et, β-d_3	80	1.033[e]	1.039	1.131	0.939	0.978
i-Pr, β-d_6	60	1.366[e]	1.237	1.181	0.925	1.132
t-Bu, β-d_9	25		1.508	1.186	0.908	1.400
n-Pr, β-d_2	80	1.054[f,d]	1.004	1.097	0.962	0.951
n-Pr, γ-d_3	80	0.921[f,d]	0.952	1.118	0.937	0.909
i-Bu, γ-d_6	95	0.958[g]	0.907	1.128	0.937	0.858
neo-Pe, γ-d_9	90	1.017[g,h]	0.851	1.163	0.921	0.794

[a] For the reaction of methyl bromide with bromide ion at 25 °C a primary ^{14}C KIE of 1.110 was also calculated, in good agreement with the range of experimental values obtained for reactions of [^{14}C]methyl iodide with various nucleophiles (M. L. Bender and D. F. Hoeg, *J. Am. Chem. Soc.*, 79, 5649 (1957)). [b] Reference 24. [c] Reference 25. [d] Anti and gauche conformers for reactant and transition state, respectively. [e] Reference 26. [f] Reference 27. [g] Reference 28. [h] Hydrolysis of neopentyl methanesulfonate.

it might be expected that any incipient carbonium ion character at C_α would be stabilized by hyperconjugation with the C_β–H bonds; consequently in the isopropyl and *tert*-butyl transition states we made allowance for the effects of hyperconjugation by following the procedure of Sims and his co-workers.[8] In each case the bond order of the C···Br partial bonds was multiplied by a constant value of 0.162 to give the amount by which the bond order of the C_α–C_β bonds was increased from unity; the decrease in bond order of each C_β–H bond was equal to one-third of this increase. Thus, for isopropyl, the resulting bond orders were $n_{\mathrm{C}\cdots\mathrm{Br}} = 0.5$, $n_{\mathrm{C-C}} = 1.081$, and $n_{\mathrm{C}_\beta\mathrm{-H}} = 0.973$, while for *tert*-butyl they were $n_{\mathrm{C}\cdots\mathrm{Br}} = 0.35$, $n_{\mathrm{C-C}} = 1.105$, and $n_{\mathrm{C}_\beta\mathrm{-H}} = 0.965$; the values of the force constants for stretching and bending were then obtained by application of eq 1 and 3, but the bond lengths were left unchanged.

Following other workers[17] we assumed that the reaction coordinate vibrational mode of each transition state could be adequately described as the asymmetric stretching motion of the making and breaking of bonds. This mode was arranged to have a zero frequency by introducing a single off-diagonal element into the otherwise diagonal force field as an interaction force constant coupling the two C···Br stretching coordinates and having a value equal to the diagonal C···Br stretching force constant. The zero frequency implies that the potential energy does not change with respect to passage along the reaction coordinate through the transition state.

The transition-state force fields for calculation of isotope effects, including all the features discussed above, are specified by the force constants contained in Table V.

Results and Discussion

Calculated KIE's for the bromine-exchange reactions are given in Table VI. For the sake of comparison, rather than expectation of close agreement, experimental KIE's determined by Robertson and his co-workers[18-22] for hydrolysis of the alkyl bromides at the same temperatures are also listed. No experimental values are available for the bromine exchanges, and, while various authors[11] have described isotope effects for second-order nucleophilic displacements of methyl halides, in general the most intensively studied reactions for a wide range of alkyl halide substrates are the pseudo-first-order solvolyses.[16] It seems likely that principles established by studies of solvolysis may be applied more generally to substitutions by nucleophiles other than solvent molecules, but there is of course a difficulty with interpretation of solvolysis data in that the mechanism cannot be directly determined by kinetic studies. We assume that solvolysis of methyl and unhindered primary bromides proceeds by the S_N2 mechanism and that borderline behavior and carbonium ion mechanisms develop with increasing substrate alkylation. In such latter cases agreement between the experimental KIE's for solvolysis and our calculated values for S_N2 bromine exchange would hardly be expected, notwithstanding the allowance for hyperconjugation in S_N2 reactions described above.

Of course, the observed KIE's are for reactions in solution whereas the calculations refer to gas-phase reactions. However, in theoretical investigations of KIE's by model calculations it has been the standard procedure to make comparisons in this way, and solvation effects have been treated explicitly only when absolutely necessary.[7] It would seem that any modifying effects of solvation on partition functions for individual molecules disappear to a good approximation when their ratios are taken for isotopic species; thus, for instance, although ideal gas expressions for translational and rotational partition functions are clearly inappropriate for species in condensed phases, it seems that the forms of their dependence on masses and moments of inertia are not altered such that simple gas-phase treatments of KIE's give results seriously in error.

Table VI also includes analyses of the calculated KIE's into the terms[23] MMI, EXC, and ZPE, such that

$$\mathrm{KIE} = (\mathrm{MMI})(\mathrm{EXC})(\mathrm{ZPE}) \qquad (6)$$

These three terms account, respectively, for the contributions from masses and moments of inertia, population of excited vibrational energy levels, and zero-point vibrational energies. Their interpretation in particular examples (such as here) is possible along the lines illustrated in the following papers.

Since there are available neither experimental KIE's for S_N2 bromine exchange with alkyl bromides nor relevant experimental data for similar S_N2 reactions for a range of temperatures, it is not valid to use these calculated KIE's by themselves to make mechanistic deductions about the reactions, because it is always possible to set up a transition-state model which reproduces an experimental KIE at one temperature.[24] *What these calculations do show is that the a priori models chosen to represent the Finkelstein transition states are not inconsistent with the best available experimental data for their calibration.* At this point we may note that inclusion of the steric factor s_ω on the CCBr

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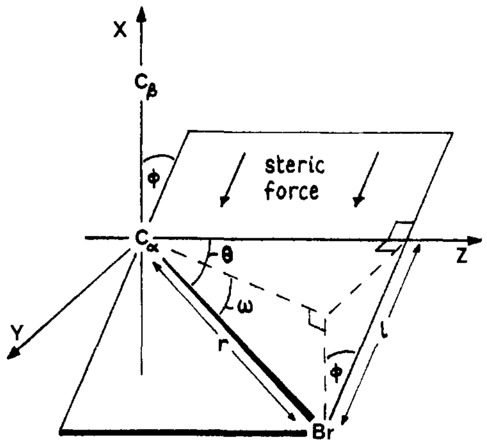

Figure 3. Distorting effect of steric force on CCBr coordinate.

bending force constants had virtually no effect on calculated KIE's. In subsequent work,[5] however, we show that this steric effect is an important feature of the model transition states and we have introduced it here for convenience.

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

Appendix. Derivation of the Steric Factor S_ω

Assume that a C_α–C_β bond and the $C_\alpha \cdots Br$ bonds would lie along the axes denoted x and z, respectively, in Figure 3 in the absence of any steric pressure. Suppose then that a perturbing steric force acts perpendicularly to the z axis distorting the C–Br bond by an angle θ from the z axis in a plane making an angle ϕ with the xz plane. There is a harmonic potential for the bending of the CCBr angle from its 90° value in the unperturbed system; the deformation ω of the CCBr coordinate is the angle between the C–Br bond and the yz plane, and the harmonic energy (per C–Br bond) of the distorted system is

$$V_b = \tfrac{1}{2}F\omega^2 \tag{7}$$

where F is the bending force constant of the undistorted system. The repulsive energy of the steric force is given by the inverse exponential expression (8), where l is the perpendicular distance

$$V_r = \alpha \exp[-\beta\,(l + l')] \tag{8}$$

of the Br atom from the z axis and α, β, and l' are constants. The total energy V of the distorted system (per C–Br bond) is $V_b + V_r$, and differentiation with respect to displacement in the CCBr coordinate gives eq 9. This derivative may be evaluated by noting

$$\frac{dV}{d\omega} = \frac{dV_b}{d\omega} + \frac{dV_r}{dl}\,\frac{dl}{d\theta}\,\frac{d\theta}{d\omega} \tag{9}$$

that $l = r \sin\theta$ and $\sin\omega = \sin\theta\cos\phi$. The equilibrium condition is given by eq 10.

$$\frac{dV}{d\omega} = F\omega - r(\cos\omega/\cos\phi)\alpha\beta \exp[-\beta(l + l')] = 0 \tag{10}$$

The force constant for bending of the CCBr coordinate in the distorted system is given by the second derivative of V with respect to ω at the equilibrium position. Thus

$$\frac{d^2V}{d\omega^2} = \frac{d^2V_b}{d\omega^2} + \frac{d^2V_r}{dl^2}\left(\frac{dl}{d\theta}\,\frac{d\theta}{d\omega}\right)^2 + \frac{d^2l}{d\theta^2}\left(\frac{dV_r}{dl}\right)\left(\frac{d\theta}{d\omega}\right)^2 + \frac{d^2\theta}{d\omega^2}\left(\frac{dV_r}{dr}\,\frac{dl}{d\theta}\right) \tag{11}$$

which when evaluated gives

$$\frac{d^2V}{d\omega^2} = F + \alpha\beta \exp[-\beta(l + l')](r(\sin\omega/\cos\phi) + \beta r^2(\cos^2\omega/\cos^2\phi)) \tag{12}$$

At equilibrium eq 10 may be substituted into eq 12, thus enabling the force constant to be expressed by eq 13. Although F is

$$F' = F(1 + \omega\tan\omega + \beta r\omega(\cos\omega/\cos\phi)) = FS_\omega \tag{13}$$

described above as the bending force constant for the undistorted system, the value substituted into eq 13 to obtain the modified force constant F' is that obtained *after* application of eq 3 using the distorted angle rather than a strictly undistorted angle. This procedure ensures that the S_ω describes the additional steric effect of longer range nonbonded interactions on CCBr bending force constants after the effects of geminal interactions on all bending force constants have been allowed for first.

NPE Effects in Bimolecular Nucleophilic Substitution

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Received December 6, 1979

Abstract: By use of the force fields established in the two preceding papers, relative NPE effects are calculated for bromide ion exchanges (the Finkelstein reactions) for a series of simple alkyl bromides. The effects on rate constants cover a range of about 30:1, neglecting contributions (if any) from variation in rotational symmetry numbers. These calculated results are analyzed in detail and compared with related literature results, both experimental and calculated. Extension of the force fields permits computation of relative NPE effects for reaction of methyl bromide with hydroxide ion and with a series of alkoxides. Effects for alkoxides differ only slightly within the group, but the NPE contribution to the rate constant for reaction with hydroxide is nearly twice that for reaction with methoxide. Interpretations for these findings are suggested.

Introduction

Bimolecular nucleophilic substitution is one of the most intensively studied reactions in organic chemistry, and it seemed particularly important to apply in this area our procedure for computation of NPE effects outlined in the two preceding papers.[1,2]

Much of the classical work on S_N2 reactions was carried out by Ingold and his collaborators,[3-5] who conducted theoretical studies, in parallel with experimental investigations, designed to provide an understanding of the role of steric, polar, and mass

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