Calculations of Steric Effects. Part II.[1] The S_N2 Halide Exchange Reactions

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Using the methods previously described, calculations have been carried out on steric effects in the S_N2 Br^-–RBr halide exchange reactions. Three transition-state models were investigated, a stiff model, a flexible model with one bond-bending mode, and a plastic model with two bond-bending modes and one bond-stretching mode. With exactly the same set of covalent radii, van der Waals radii, and nonbonded potential functions that were used before, the increments $\delta\Delta G$ [$=\Delta G^‡(\mathrm{R}) - \Delta G^‡(\mathrm{Me})$], $\delta\Delta H^‡$, and $\delta\Delta S^‡$ were well reproduced by the flexible and plastic models for R = Et, Pr^i, Bu^t, Pr^n, Bu^i, and neopentyl. The most significant difference between results of the present calculations and those of Ingold and his co-workers in 1955 is that we are able to account for the observed values of the activation parameters purely in terms of steric effects, whereas in Ingold's calculations substantial polar effects of α-groups in the transition state were postulated to take place. It is shown that the necessity for the assumption of polar effects arises from the method of calculation of the nonbonded interactions.

PREVIOUSLY,[1] we have calculated steric effects of alkyl groups, R, on rate constants for the S_E2 reaction (**1**), a substitution known to proceed with retention of configuration for the case of R = Bu^s. Since our method of

$$\mathrm{RHgX} + \overset{*}{\mathrm{Hg}}\mathrm{X_2} \longrightarrow \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{HgX_2} \qquad (1)$$

calculation involved a number of novel features, and since the nonbonded potential functions that we used had not hitherto been employed in such rate calculations, we thought it advisable to undertake the calculation of steric effects on a totally different system in order to test the validity of the general method and the functions used. We chose the symmetrical halide exchange reaction (2) for a number of reasons. First, the stereochemistry and mechanism of reaction (2) are well defined, and the known

$$\mathrm{Br^-} + \mathrm{RBr} \longrightarrow \mathrm{BrR} + \mathrm{Br^-} \qquad (2)$$

inversion of S_N2 reactions should provide an interesting

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[1] Part I, M. H. Abraham, P. L. Grellier, and M. J. Hogarth, *J.C.S. Perkin II*, 1974, 1613.

contrast to the retention observed in reaction (1). Secondly, although the halide exchange reactions have been extensively investigated by Ingold and his co-workers,[2,3] who carried out detailed calculations on steric effects, the results of Ingold have not been universally accepted; the experimental results have been subject to criticism (see later), and the actual calculations are so cumbersome that few workers have felt able to discuss the method of calculation in any detail. We felt that a more direct calculation of steric effects in reaction (2) was timely, especially as that further experimental results on the halide exchange reactions are now available.

There is no doubt that the calculations of Ingold[3] on reaction (2) yield rate constants, relative to $k^{\mathrm{Me}} = 1$, that are in substantial agreement with experiment.[4] However, there are a number of unsatisfactory features in the calculations. There are incorporated in the calculations a large number of parameters, some of which are adjustable and some of which are estimated. More seriously, agreement between calculation and experiment is achieved only by the inclusion of polar factors arbitrarily weighted as 1 kcal for R = n-alkyl, 2 kcal for R = s-alkyl, and 3 kcal for R = t-alkyl. For example, values of $\delta\Delta H^{\ddagger}$ for reaction (1) were calculated as in Table 1,[3] where ΔW_{s} is the calculated steric effect and ΔW_{p} the assumed polar effect. In these cases, the assumed polar term (ΔW_{p}) makes the major contribution to $\delta\Delta H^{\ddagger}$ (calc.) and substantial contributions (40%) to $\delta\Delta G^{\ddagger}$ (calc.). We hoped that our own calculations might help to resolve this problem of the assumed polar effect.

TABLE 1

Steric and polar effects in Ingold's[3] calculations

R	Me	Et	Pr$^{\mathrm{i}}$
ΔW_{s}/kcal mol^{-1}	0	0.8	1.6
ΔW_{p}/kcal mol^{-1}	0	1	2
$\delta\Delta H^{\ddagger}$ (calc.)	0	1.8	3.6
$\delta\Delta H^{\ddagger}$ (obs.)	0	1.7	3.9
$\delta\Delta G^{\ddagger}$ (calc.)	0	2.4	4.7
$\delta\Delta G^{\ddagger}$ (obs.)	0	2.6	5.2

Theory of the Method.—Since we have discussed[1] our method of calculation fully, and since the method is applied here in its entirety, we give now only an outline of the method with respect to its application to reaction (2). The procedure used falls into two clear parts. In the first part, the geometry of a transition state is defined and distances between nonbonded atoms or groups then calculated. Nonbonded potential functions are set up that relate the energy of interaction to internuclear distance and the various nonbonded interactions are obtained, after suitable corrections for the non-spherical shape of a methyl group and for shielding by intervening atoms. Rotation of groups is allowed, and calculations are carried out until the position of minimum energy ($E^{\ddagger}_{\mathrm{min}}$) is found. A similar calculation is carried out for the initial state (in this case RBr) to yield the term $E^{\mathrm{i}}_{\mathrm{min}}$, and the effect of these terms on the rate constant is given by $E = \exp[-(E^{\ddagger}_{\mathrm{min}} - E^{\mathrm{i}}_{\mathrm{min}})/RT]$. This simple expression holds because interactions in MeBr and in the transition state [BrMeBr]‡ are small enough to be taken as zero.

Where rotation is not completely free, the above procedure also yields the energy profile for rotation. In the second part of the calculation the effect of such restricted rotation on the rate constant is determined by calculating the average angle of rotation of a set of molecules in the potential well; the rotational factor is then given by F = average angle of rotation/360, since for completely free rotation the rotational angle is 360°: These rotational factors are determined for initial-state and transition-state rotation of β-methyl groups [R = Pr$^{\mathrm{n}}$, Bu$^{\mathrm{i}}$, and neopentyl (Pe$^{\mathrm{neo}}$)], and also for transition-state rotation of α-methyl groups in certain circumstances. The final expression for the rate factors $k^{\mathrm{R}}/k^{\mathrm{Me}}$ is given by equation

$$k^{\mathrm{R}}/k^{\mathrm{Me}} = FE = \frac{F^{\ddagger}{}_{\alpha} \,.\, F^{\ddagger}{}_{\beta}}{F^{\mathrm{i}}{}_{\beta}} \exp\,[\,-(E^{\ddagger}{}_{\mathrm{min}} - E^{\mathrm{i}}{}_{\mathrm{min}})/RT] \qquad (3)$$

(3). The rotational factors are all unity for the initial state MeBr and the transition state [BrMeBr]‡.

In all our calculations we have used the covalent radii, van der Waals radii, and nonbonded potential functions tabulated before.[1] We set out the experimental observations of reaction (2), and then give the results of our calculations in order of increasing complexity of the transition state model adopted. To avoid rather large rate factors we recast equation (3) as (4) where $\delta\Delta G^{\ddagger}$ (cal mol^{-1}) is defined as $\Delta G^{\ddagger}(\mathrm{R}) - \Delta G^{\ddagger}(\mathrm{Me})$.

$$\delta\Delta G^{\ddagger} = (E^{\ddagger}{}_{\mathrm{min}} - E^{\mathrm{i}}{}_{\mathrm{min}}) - 1\,364 \log\left(\frac{F^{\ddagger}{}_{\alpha}F^{\ddagger}{}_{\beta}}{F^{\mathrm{i}}{}_{\beta}}\right) \qquad (4)$$

Since initial state effects are the same throughout, we first summarise in Table 2 the terms $E^{\mathrm{i}}{}_{\mathrm{min}}$ and $F^{\mathrm{i}}{}_{\beta}$ for the various alkyl bromides studied.

TABLE 2

Calculated initial state effects (E/cal mol^{-1}) for alkyl bromides at 298 K

	Me	Et	Pr$^{\mathrm{i}}$	Bu$^{\mathrm{t}}$	Pr$^{\mathrm{n}}$	Bu$^{\mathrm{i}}$	Pe$^{\mathrm{neo}}$
α-Me–Br interaction	0	85	170	255	85	85	85
β-Me–Br interaction					−296	−362	−48
$E^{\mathrm{i}}{}_{\mathrm{min}}$	0	85	170	255	−211	−277	37
$F^{\mathrm{i}}{}_{\beta}$					0.651	0.396	0.245

Experimental Observations.—Rate constants for the Br^{-}–RBr reaction and for several other halide exchanges were obtained by Ingold and his co-workers, using acetone solvent.[2,3,5] The various experimental results have been criticised (see ref. 4) chiefly because (i) the lithium halides used as the source of the halide ions are only weak electrolytes in acetone, and (ii) the results for the so-called $S_{\mathrm{N}}2$ exchanges of t-butyl halides in acetone are erroneous since these reactions are not $S_{\mathrm{N}}2$ substitutions at all, but proceed by an elimination–addition mechanism. More recently, Cook and Parker[4] have re-investigated the Cl^{-}–RBr reaction using solvent dimethylformamide

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[2] I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1946, 173.

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

[4] D. Cook and A. J. Parker, *J. Chem. Soc.* (*B*), 1968, 142.

[5] P. B. D. de la Mare, *J. Chem. Soc.*, 1955, 3180.

(DMF) under conditions such that the above criticisms are rendered nugatory. In particular, they obtained the true rate constant for the S_N2 exchange Cl^-–Bu^tBr so that it is now possible to assess the steric effect of the Bu^t group, in terms of the σ-values defined by equation (5). The change of solvent from acetone to DMF has no

$$\sigma = \log k^{Me} - \log k^{R} \qquad (5)$$

great effect on the σ values, as can be seen for the Cl^-–RBr reaction (Table 3). A plot of σ in DMF against σ in acetone yields a good straight line except for the point for R = Pe^{neo}, where the recent work indicates a value of 6.92 in acetone rather than the quoted value of 6.37.

TABLE 3

σ Values for S_N2 reactions of alkyl halides

Reaction	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	Pe^{neo}
Average values [7]	0	1.31	2.92	4.40 [a]	1.67	2.70	6.18
Average values [6]	0	1.5	3.1	4.6 [a]	1.9	3.0	6.5
Br^-–RBr in acetone [5]	0	1.88	3.84	5.50 [a,b]	2.07	3.36	7.70, [a] 6.70
Cl^-–RBr in DMF [4]	0	1.57	3.31	4.66	1.73	3.05	6.77
Cl^-–RBr in acetone [c]	0	1.79	3.67	4.76 [a,b]	1.97	2.61	6.92, [a] 6.37

[a] Calculated from σ values for the Cl^-–RBr reaction in DMF. [b] The originally reported values refer to elimination–addition reactions. [c] E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *J. Chem. Soc.*, 1955, 3173.

TABLE 4

Observed activation parameters for the Br^-–RBr exchange in acetone

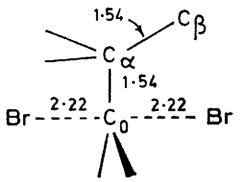
	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	Pe^{neo}
σ-Value (Table 3)	0	1.88	3.84	5.50	2.07	3.36	7.70
$\delta\Delta G^{\ddagger}$/kcal mol^{-1}	0	2.56	5.24	7.50	2.82	4.58	10.50
$\delta\Delta H^{\ddagger}$/kcal mol^{-1}	0	1.7	3.9	8.0 [a]	1.7	3.1	9.0 [a]
$\delta\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	0	−2.7	−4.6	+1.7 [a]	−4.1	−5.0	−5.0 [a]

[a] Estimated from data on the Cl^-–RBr exchange (see text).

There are also good linear relationships between the σ values of Streitwieser [6] and of Okamoto [7] and those for the Cl^-–RBr reaction in DMF, from which σ values for the Bu^t group may be calculated (Table 3). Also in Table 3 are the experimental data [3,5] for the Br^-–RBr reaction in acetone; again there is a good linear relation with σ values for the Cl^-–RBr reaction in DMF from which a value for the Bu^t group can be found, and from which a revised value for the Pe^{neo} group can be calculated.

It is not so easy to estimate the correct $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values for the Br^-–RBr reaction in acetone for the Bu^t (and also the Pe^{neo}) group.* Cook and Parker [4] give $\delta\Delta H^{\ddagger}$ a value of 7.6 kcal mol^{-1} for the Cl^-–Bu^tBr exchange in acetone, but a value of only 3.3 kcal mol^{-1} for the corresponding exchange in DMF, even though there is good agreement for most alkyl groups between the two solvents. There is also a discrepancy, although smaller, for the Cl^-–$Pe^{neo}Br$ exchange, $\delta\Delta H^{\ddagger}$ being 6.0 in acetone and 8.4 kcal mol^{-1} in DMF. In Table 4 we give what we consider to be the most reasonable values of $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ for the Br^-–RBr reaction.

The 'Stiff' Transition-state Model.—The simplest transition state for the S_N2 reaction (2) is the stiff model shown in Scheme 1. No bond-bending or -stretching is allowed, although rotation about the C_α–C_0 axis is permitted. Since we have fixed the various nonbonded potential functions, the only adjustable parameter is the $C_0 \cdots Br$ partial bond length. We took this length at 2.22 Å, close to the value of 2.25 Å used by Ingold *et al.*[2] in their calculations on a stiff transition-state model, and the average of the partial bond lengths used in our own calculations on the plastic model. In Table 5 we summarise results of our calculations; as well as the direct quantity $E^{\ddagger}_{min}$, there are also rotational restrictions ($F^{\ddagger}_{\beta}$) of the β-methyl groups as they eclipse the bromine atoms in the transition state.



SCHEME 1 The stiff transition-state model

The calculated values of $\delta\Delta G^{\ddagger}$ show surprisingly good agreement with experiment, except for the hindered alkyl groups Bu^i and Pe^{neo}. Thus, as we found in our calculations before,[1] a stiff transition state model is quite realistic when steric effects are not too large. The stiff model, however, does not reproduce the observed values of $\delta\Delta H^{\ddagger}$ very well. It is of interest that our calculated values of $\delta\Delta H^{\ddagger}$ are generally too high, whereas Ingold's calculated values are generally too low.

The 'Flexible' Transition-state Model.—In order to obtain better agreement with experiment than was possible with the stiff model, Ingold [3] carried out calculations on an 'elastic' model in which the $C_0 \cdots Br$ partial bonds were allowed to stretch. His results using the elastic model, in terms of $\delta\Delta H^{\ddagger}$ (calc.), were not very different from those with the stiff model, however, and so we

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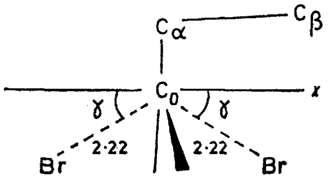
* $\delta\Delta H^{\ddagger} = \Delta H^{\ddagger}(RX) - \Delta H^{\ddagger}(MeX)$, and $\delta\Delta S^{\ddagger} = \Delta S^{\ddagger}(RX) - \Delta S^{\ddagger}(MeX)$.

[6] A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 571.

[7] K. Okamoto, I. Nitta, T. Imoto, and H. Shingu, *Bull. Chem. Soc. Japan*, 1967, **40**, 1905.

turned to a model that allows bond-bending but not bond-stretching. We term this a flexible model, shown in Scheme 2. In the flexible model, the Br$\widehat{C}_0$Br angle is allowed to vary from 180° to an angle $(180-2\gamma)°$ where γ is defined in Scheme 2.* Since the $C_0 \cdots Br$ partial bonds are the weakest bonds in the transition state, the energy required to bend the $Br \cdots C_0 \cdots Br$ bonds should be comparatively small. We took a bending force constant (k/r^2) of 0.055×10^5 dyn cm^{-1}, that is about half the force constant for the Br–B–Br bend (0.13×10^5) and about a quarter of that for the Br–C–Br bend (0.24×10^5).[8] Any Me–Br interaction that is lowered by bond-bending is counteracted to some extent by the energy required to bend the bond, and the sum total must be minimised in order to derive the value of $E^‡_{min}$.



SCHEME 2 The flexible transition-state model

Rotation of β-methyl groups around the C_α–C_0 axis will be restricted because of the energy barrier to the eclipse of the bromine atoms ($F^‡_\beta$), but in addition there will also be a (small) energy barrier to rotation of α-methyl groups around the C_0–x axis, since the C_α–Br distance changes with α-rotation.

Results obtained with the flexible model are in Table 6. The various interactions that lead to $E^‡_{min}$ are given, as well as the transition state rotational factors. Agreement between the calculated and observed parameters is now good, not only for $\delta\Delta G^‡$ but also for $\delta\Delta H^‡$ and $\delta\Delta S^‡$. Thus the incorporation of the BrC_0Br bond bending into the calculations very considerably improves the agreement. Even for the hindered cases, R = Bu^t, Bu^i, and Pe^{neo}, the observed activation parameters are quite well reproduced, the only discrepancies of any note being in the calculated $\delta\Delta H^‡$ and $\delta\Delta S^‡$ values for the Pe^{neo} group. Just as in the simple case of the stiff model, we have not had to introduce any polar factors in order to obtain agreement with experiment. This could, of course, be an artifact due to our use of a flexible model whereas Ingold's assumed polar terms were incorporated into calculations based on a plastic model. We felt it obligatory, therefore, to repeat the calculations using a plastic model close to the type of transition state model used by Ingold.

TABLE 5

Calculations using the stiff transition state model, with $C_0 \cdots Br$ fixed at 2.22 Å. Energies are in cal mol^{-1}, and all data are at 298 K

	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	Pe^{neo}
$E^‡_{min}$	0	2 696	5 269	7 719	2 140	6 330	>57 000
$E^‡_{min} - E^i_{min}$	0	2 611	5 099	7 464	2 351	6 611	>57 000
$F^‡_\beta$					0.218	0.0758	?
$F^‡_\beta/F^i_\beta$					0.335	0.191	
$\delta\Delta G^‡$ (calc.)	0	2 610	5 100	7 460	3 000	7 590	>57 000
$\delta\Delta G^‡$ (obs.)	0	2 560	5 240	7 500	2 820	4 580	10 500
$\delta\Delta H^‡$ (calc.)	0	2 610	5 100	7 460	2 350	6 610	>57 000
$\delta\Delta H^‡$ (obs.)	0	1 700	3 900	~8 000	1 700	3 100	~9 000
$\delta\Delta H^‡$ (calc. ref. 3)	0	900	1 900	2 800	900	2 800	13 900

TABLE 6

Calculations using the flexible transition state model, with $C_0 \cdots Br$ fixed at 2.22 Å. Energies are in cal mol^{-1}, and all data are at 298 K

Interaction	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	Pe^{neo}
α-Me–Br		1 031	3 128	8 088	1 031	450	−312
β-Me–Br					−590	598	3 128
α-Me–α-Me			−123	−369			
Bond bending [γ(°)]		595(5)	856(6)	0(0)	595(5)	1 522(8)	7 702(18)
$E^‡_{min}$	0	1 626	3 861	7 719	1 036	2 570	10 518
$E^‡_{min} - E^i_{min}$	0	1 541	3 691	7 464	1 247	2 847	10 481
$F^‡_\alpha$		0.294	0.167		0.294	0.270	0.292
$F^‡_\beta$					0.264	0.105	0.680
$F_\alpha^‡F^‡_\beta/F^i_\beta$	(1)	0.294	0.167	(1)	0.119	0.0715	0.812
$\delta\Delta G^‡$ (calc.)	0	2 270	4 750	7 460	2 510	4 410	10 600
$\delta\Delta G^‡$ (obs.)	0	2 560	5 240	7 500	2 820	4 580	10 500
$\delta\Delta H^‡$ (calc.)	0	1 540	3 690	7 460	1 250	2 850	10 480
$\delta\Delta H^‡$ (obs.)	0	1 700	3 900	~8 000	1 700	3 100	~9 000
$\delta\Delta S^‡$ (calc.)	0	−2.4	−3.6	0.0	−4.2	−5.2	−0.4
$\delta\Delta S^‡$ (obs.)	0	−2.7	−4.6	~1.7	−4.1	−5.0	~−5.0

The Plastic Transition-state Model.—The flexible model (Scheme 2) is used as a basic, but the $C_0 \cdots Br$ partial bond is now allowed to stretch from an equilibrium distance that we take as 2.19 Å. We estimated a value for the stretching force constant of 1.8×10^5 dyn cm^{-1}, rather less than the value of 2.8×10^5 dyn cm^{-1} for a normal C–Br stretch.[8] Since the stretching energy terms turn out to be quite small, the actual value of the force constant chosen is not critical. In the flexible model, the

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* Note that the C_α group need not be positioned as shown in Scheme 2, but is allowed to rotate about the x-axis until the total transition state energy is a minimum.

[8] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

Br $\cdots$ C_0 $\cdots$ Br bonds were allowed to bend in the *xy*-plane by an angle γ, corresponding to the distance Δy in Scheme **3**. The plastic model incorporates another bending mode, this time along the *z*-axis, by an angle θ, corresponding to a distance Δz.* As before, we took a bending force constant of 0.055×10^5 dyn cm^{-1} for the γ- and θ-bends.

Calculations in terms of the plastic model are much more complicated than those with the flexible model, since the transition state energy now has to be minimised with respect to the C_0 $\cdots$ Br stretch, two bond-bending modes, and the Me–Br interactions that take place as α- and β-rotation occurs. The various interactions that make up the value of $E^{\ddagger}_{\text{min}}$ are summarised in Table 7. The second bending mode is of consequence only in the Pe$^{\text{neo}}$ transition state, when a bend $\theta = 6°$ reduces the transition state energy by *ca.* 900 cal mol^{-1}. For most of the transition states, the values of $E^{\ddagger}$ are not very sensitive to the values of γ, θ, and the C_0 $\cdots$ Br length in the transition state. As an example (Table 8), we give the calculated values of $E^{\ddagger}$ for the Pe$^{\text{neo}}$ transition state as a function of γ and the C $\cdots$ Br length when θ is fixed at zero. For $\theta = 0°$, the energy is minimised at 10 636 cal mol^{-1} when the C_0 $\cdots$ Br length is 2.21 Å and $\gamma = 17°$; naturally, in order to find the true minimum energy, $E^{\ddagger}_{\text{min}}$, these calculations are repeated for various values of θ. A similar flat energy surface to the above also occurs with respect to θ, the combinations $\gamma = 14°$, $\theta = 7°$, and $\gamma = 16°$, $\theta = 5°$ yielding valuesof $E^{\ddagger}$ only *ca.* 100 cal mol^{-1} higher than the $E^{\ddagger}_{\text{min}}$ value that occurs when $\gamma = 15°$, $\theta = 6°$ (in these three calculations the C_0 $\cdots$ Br length was 2.21 Å).

TABLE 7

Calculations using the plastic transition state model. Energies are in cal mol^{-1}, and all data are at 298 K.

	Me	Et	Pr$^{\text{i}}$	Bu$^{\text{t}}$	Pr$^{\text{n}}$	Bu$^{\text{i}}$	Pe$^{\text{neo}}$
C_0 $\cdots$ Br length (Å)	2.19	2.20	2.21	2.24	2.20	2.20	2.21
Bond angle γ (°)	0	5	6	0	5	8	15
Bond angle θ (°)	0	0	0	0	0	0	6
Interaction							
α-Me–Br		1 140	3 244	7 494	1 140	524	−170
β-Me–Br					−593	672	3 580
α-Me–α-Me			−123	−369			
C_0 $\cdots$ Br stretch		25	104	648	25	25	104
Bond bending [γ(°)]		595	856		595	1 522	5 348
Bond bending [θ(°)]							856
$E^{\ddagger}_{\text{min}}$	0	1 760	4 081	7 773	1 167	2 743	9 718
$E^{\ddagger}_{\text{min}} - E^{\text{i}}_{\text{min}}$	0	1 675	3 911	7 518	1 378	3 020	9 681
$F^{\ddagger}_{\alpha}$		0.292	0.164		0.292	0.261	0.285
$F^{\ddagger}_{\beta}$					0.255	0.109	0.215
$F^{\ddagger}_{\alpha}F^{\ddagger}_{\beta}/F^{\text{i}}_{\beta}$	(1)	0.292	0.164	(1)	0.0744	0.0284	0.0613

TABLE 8

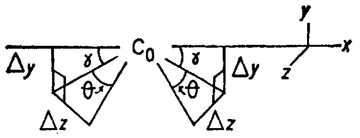
C_0 $\cdots$ Br (Å)		2.20	2.21	2.22	2.23
		$E^{\ddagger}$/cal mol^{-1}			
γ(°)	16	10 764	10 715	10 717	10 773
	17	10 675	10 636	10 648	10 724
	18	10 739	10 720	10 750	10 844

TABLE 9

Calculated and observed activation parameters for the Br$^-$–RBr exchange using the plastic transition state model

	Me	Et	Pr$^{\text{i}}$	Bu$^{\text{t}}$	Pr$^{\text{n}}$	Bu$^{\text{i}}$	Pe$^{\text{neo}}$
$\delta\Delta G^{\ddagger}$ (calc.), this work	0	2 410	4 980	7 520	2 660	4 580	10 500
$\delta\Delta G^{\ddagger}$ (calc.), ref. 3	0	2 410	4 720	5 840	2 800	4 720	10 140
$\delta\Delta G^{\ddagger}$ (obs.)	0	2 560	5 240	~7 500	2 820	4 580	~10 500
$\delta\Delta H^{\ddagger}$ (calc.), this work	0	1 700	3 900	7 500	1 400	3 000	9 700
$\delta\Delta H^{\ddagger}$ (calc.), ref. 3	0	1 800	3 600	5 500	1 800	3 300	8 300
$\delta\Delta H^{\ddagger}$ (obs.)	0	1 700	3 900	~8 000	1 700	3 100	~9 000
$\delta\Delta S^{\ddagger}$ (calc.), this work	0	−2.4	−3.6	0.0	−4.3	−5.2	−2.7
$\delta\Delta S^{\ddagger}$ (calc.), ref. 3	0	−2.1	−3.8	−1.1	−3.3	−4.7	−6.3
$\delta\Delta S^{\ddagger}$ (obs.)	0	−2.7	−4.6	~+1.7	−4.1	−5.0	~−5.0

ΔG, ΔH in cal mol^{-1}, ΔS in cal mol^{-1} K^{-1}.



SCHEME 3 The bending modes in the plastic transition-state model.

DISCUSSION

The breakdown of transition state steric effects, in terms of the plastic model, is in Table 7, and the calculated activation energies are compared with the observed values in Table 9. In all the plastic transition states, provision of stretching has increased the length of the C_0 $\cdots$ Br bond from its equilibrium value of 2.19 Å. The increases are all quite small, that in the Bu$^{\text{t}}$ transition state being the largest (0.05 Å). Of the terms that make up the

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* It is convenient to consider the two bending modes separately, although the angles γ and θ could be combined to yield a resultant angle. In practice, the second bending mode (θ) is of consequence only for the Pe$^{\text{neo}}$ group, when $\gamma = 15$ and $\theta = 6°$, giving bending energies of 5 348 and 856 (total 6 204 cal mol^{-1}). In this case, the resultant angle may be calculated as 16° 8′, giving a bending energy of 6 187 cal mol^{-1}. The difference between 6 204 and 6 187 cal mol^{-1} is so small as to be quite insignificant.

value of $E^{\ddagger}_{\min}$, the α-Me–Br interactions are by far the largest in the Et, Pr^i, and Bu^t transition states. The situation in the β-methylated series ($R = Pr^n$, Bu^i, and Pe^{neo}) is not so clearcut, with terms due to bond-bending now making major contributions to $E^{\ddagger}_{\min}$. Rotational factors also influence the final rate factors markedly with both β-rotation around the C_α–C_0 axis, and α-rotation around the x-axis contributing. In the case of the Bu^t transition state, the angle γ is effectively 0° since any deviation of the bromine atoms by a distance Δy greatly increases the α-Me–Br interaction. For the other transition states, the α-Me groups (or α-groups) can be positioned so that α-group–Br interactions are decreased with increase in γ. Similarly the angle θ is zero (except for the Pe^{neo} case) because the sideways movement of the bromine atoms by a distance Δz usually results in a net increase in the interaction of the alkyl groups with the bromine atoms; only for the Pe^{neo} transition state does a movement Δz decrease the net steric interactions.

When our three sets of calculations are compared with the experimental observations, it is seen that although there is a marked improvement on changing from the stiff model to the flexible model, especially for the Bu^i and Pe^{neo} calculations, results from the flexible and plastic models are quite similar. Thus in view of the much more complex calculations using the plastic model, we feel that the flexible model provides the best compromise between results obtained and time of computation. Where steric effects are not too large, the very simple stiff model yields reasonable results, especially in terms of $\delta\Delta G^{\ddagger}$. There seems little point using any model more complex than the plastic model; any further refinement we think would affect the calculated $\delta\Delta G^{\ddagger}$ values only marginally and would alter the calculated $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values probably only in the Pe^{neo} case. In general, the agreement between the calculated and observed activation parameters (Table 9) is good enough to render further refinement unnecessary. Using our approach, the observed values of $\delta\Delta H^{\ddagger}$ arise through nonbonded interactions in the transition states, and the values of $\delta\Delta S^{\ddagger}$ (obs.) through restricted rotation of groups in the transition state. Initial state effects, although taken into account, are rather small (Table 2).

As far as our original intention is concerned, we have shown that the methods used previously[1] to calculate steric effects in the S_E2 (Ret) reaction (1) can be applied successfully to calculate steric effects in the S_N2 (Inv) reaction (2), using exactly the same covalent radii, van der Waals radii, and nonbonded potential functions. To our knowledge, this is the first time that one set of nonbonded functions has been used to calculate steric effects in transition states that are geometrically quite different. Since the above radii and functions were taken as fixed at the start of our calculations, we have been left with a minimum of adjustable and empirical parameters. In calculations using the stiff model, the only such parameter we used was the $C_0 \cdots Br$ bond length, taken as an average of 2.22 Å.* With the flexible model, two parameters were used, the $C_0 \cdots Br$ bond length and the $Br \cdots C_0 \cdots Br$ bond-bending constant. Even with the plastic model, we used only three parameters, the $C_0 \cdots Br$ equilibrium bond length of 2.19 Å, the $Br \cdots C_0 \cdots Br$ bond-bending constant, and the $C_0 \cdots Br$ stretching force constant. With these three parameters, we could account for the 18 values of $\delta\Delta G^{\ddagger}$, $\delta\Delta H^{\ddagger}$, and $\delta\Delta S^{\ddagger}$, of which 12 are independent parameters.

Finally, we compare our calculations using the stiff model (Table 5) and the plastic model (Table 9) with those of Ingold[3] using similar models. Our stiff model, although giving reasonable values of $\delta\Delta G^{\ddagger}$, generally yields $\delta\Delta H^{\ddagger}$ values that are too high, whereas Ingold's calculations yield $\delta\Delta H^{\ddagger}$ values that are generally too low. For the two sets of calculations on the plastic model, there is good agreement with experiment in both cases, and there is little point in attempting to select the 'best' set of calculations. Although both sets of calculations give $\Delta H^{\ddagger}$ values that are close to those observed experimentally, there is considerable difference between the sets in terms of the origin of the $\delta\Delta H^{\ddagger}$ values. Let us take the values for the Bu^t transition state as an example. Our value of 7.5 kcal mol^{-1} is composed entirely of steric effects, the sum total of transition state steric effects, including nonbonded interactions and bond stretching, being 7.8 kcal mol^{-1}, and initial state steric effects being 0.3 kcal mol^{-1}. On the other hand, Ingold's value of 5.5 kcal mol^{-1} is composed of steric effects (only 2.5 kcal mol^{-1}) plus a large contribution from polar effects (3 kcal mol^{-1}). This is in line with results on the simple stiff model, where our $\delta\Delta H^{\ddagger}$ (calc.) values are also much higher than Ingold's. Since the only real justification for incorporation of polar effects is the agreement between theory and experiment so provided, our calculations thus lead to the conclusions that there is no need to postulate polar effects at all.† This conclusion is of interest enough to warrant further investigation on the origin of the calculated $\delta\Delta H^{\ddagger}$ values. First, there are small but possibly significant differences in the geometry of the plastic transition states; our $C_0 \cdots Br$ bond length is 2.24 Å in the Bu^t transition state, whereas the $C_0 \cdots Br$ distance is 2.29 Å on Ingold's geometry.[3] If we used the latter distance in the Bu^t transition state (corresponding to an equilibrium distance of 2.25 Å), our value of $\delta\Delta H^{\ddagger}$ (calc.) would be lowered by 1.3 kcal mol^{-1} to give $\delta\Delta H^{\ddagger}$ (calc.) as 6.2 kcal mol^{-1}, still very much larger than Ingold's steric interaction of 2.5 kcal mol^{-1}. The second difference between the calculations to give $\delta\Delta H^{\ddagger}$ lies in the computation of the nonbonded interactions; we have taken the methyl

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* This is the average of the various $C_0 \cdots Br$ bond lengths in the plastic models, after stretching from 2.19 Å to the values in the transition states (2.20—2.24 Å).

† Evans has previously suggested[9] that constitutional effects of alkyl groups in S_N2 reactions are steric in origin. This conclusion, however, was based on qualitative arguments and was not supported by quantitative studies; in the only quantitative calculation given, Evans found that for the I^-–RI reaction, $\delta\Delta H^{\ddagger}$ was *ca.* 2 kcal mol^{-1} for $R = Bu^t$ whereas the observed value is probably nearer to 8 kcal mol^{-1}.

[9] A. G. Evans, *Trans. Faraday Soc.*, 1946, **42**, 719.

group as a single entity and in the Bu^t transition state calculate, for example, the Me–Br interactions, whereas Ingold calculates the various C–Br and H–Br interactions separately. It is not possible to assess exactly the effect of these two procedures in a given example, since Ingold does not give a break-down of the total steric effect (2.5 kcal mol^{-1}) into its component interactions, but it seems reasonably certain that the different calculated values of $\delta\Delta H^\ddagger$ arise mainly through the different nonbonded potential functions employed.

It is not our intention to criticise the procedure and functions used by Ingold,[3] but merely to point out that the conclusion that polar effects operate in these S_N2 reactions depends almost entirely on the way the nonbonded interactions in the transition states are calculated. Ingold's methods lead to very small calculated steric effects, especially in the α-methylated series, so that a polar transition state factor is required in order to obtain agreement with experiment. Our method leads to calculated steric effects of about the correct magnitude, so that no polar factors are needed. On the plastic model, the two procedures yield the values in Table 10 for $\delta\Delta H^\ddagger$.

It is therefore arguable whether or not there is a polar transition state effect in operation in the S_N2 halide exchange reactions. From our own calculations we conclude that a polar effect is not present, but other workers may assess differently the evidence that we have here presented.

TABLE 10

Comparison of calculations of $\delta\Delta H^\ddagger$ for the Br^-–RBr exchange

	Me	Et	Pr^i	Bu^t	Pr^n	Bu^i	Pe^{neo}
Ingold's calc.							
Calculated steric effect	0	0.8	1.6	2.5	0.8	2.3	7.3
Assumed polar effect	0	1.0	2.0	3.0	1.0	1.0	1.0
Total $\delta\Delta H^\ddagger$ (calc.) [3]/kcal mol^{-1}	0	1.8	3.6	5.5	1.8	3.3	8.3
This work							
Calculated steric effect $=\delta\Delta H^\ddagger$ (calc.)/kcal mol^{-1}	0	1.7	3.9	7.5	1.4	3.0	9.7
$\delta\Delta H^\ddagger$ (obs.)/kcal mol^{-1}	0	1.7	3.9	8.0	1.7	3.1	9.0

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