Calculations of Steric Effects. Part I. Uncatalysed S_E2 Substitution of Alkylmercury(II) Salts by Mercury(II) Salts in Ethanol

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Steric effects of alkyl groups in reaction (1) have been calculated by setting up nonbonded potential functions

$$\text{RHgX} + \text{HgX}_2 \xrightarrow{\text{EtOH}} \text{RHgX} + \text{HgX}_2 \qquad (1)$$

and obtaining the various nonbonded interaction energies in both initial states and transition states. These interactions lead to restricted rotation of methyl groups both in the initial state (β-rotation) and transition state (α- and β-rotation), and a treatment is given that allows the effect of restricted rotation on the relative rate constants to be determined. Calculations carried out on an open transition state model lead to close agreement between observed and calculated relative rate constants for R = Me, Et, and Bu^tCH_2 (X = Br at 100°) and for R = Me and Bu^s (X = OAc at 60°), viz. observed (Me : Et : Bu^tCH_2 : Bu^s), 1 : 0·42 : 0·33 : 0·06 and calculated, 1 : 0·50 : 0·38 : 0·05, and it is shown that the above sequence is mainly due to the effect of restricted rotation of groups in the transition state. Similar calculations carried out using a cyclic transition state model do not yield relative rate constants that are at all compatible with the observed relative rates.

CONSTITUTIONAL effects of alkyl groups on the rates of S_E2 reactions have been the subject of considerable discussion. In substrates of the type RMX_n (where R is the alkyl group undergoing substitution, M is a metal atom, and X_n are atoms or alkyl groups attached to the leaving atom M) it now seems [1] for S_E2 reactions proceeding through open transition states that constitutional effects of the moving alkyl group R are much larger than those of the leaving alkyl groups X. It has often been suggested that such constitutional effects of the moving alkyl group R are steric in origin, in the case of S_E2(open) reactions involving retention of configuration [1-4] and inversion of configuration [5] at the carbon atom undergoing substitution. Furthermore, it has been claimed that comparison of the reactivity sequence in a set of alkyls RMX_n, as R is varied, with typical S_N2 reactivity sequences of alkyl halides will serve to differentiate between S_E2(open) reactions proceeding with inversion from those proceeding with retention of configuration, since steric effects in the two geometrically dissimilar types of transition state will not be the same.[4,5]

Although Hughes and Volger [2] carried out rough calculations to show that in reaction (1) there was sufficient steric compression in the transition state to account for the relative reactivities of the substrates RHgX (R = Me, Et, Bu^tCH_2, and Bu^s), there have been no detailed calculations carried out to support the contention that constitutional effects in S_E2(open) reactions are indeed steric in origin. We report here the results of calculations of steric effects in the simple uncatalysed

mercury-for-mercury exchange (1), and give a general outline of the method used.

$$\text{RHgX} + \overset{*}{\text{Hg}}\text{X}_2 \xrightarrow{\text{EtOH}} \text{R}\overset{*}{\text{Hg}}\text{X} + \text{HgX}_2 \qquad (1)$$

Theory of the Method.—The first part of the calculation follows the general scheme used by Ingold [6,7] in his calculation of steric effects in the S_N2 reaction. A transition state model is chosen, the distances in the transition state between nonbonded atoms are calculated by simple geometry, and interactions between the nonbonded atoms are then deduced through nonbonded potential functions that relate interaction energy to nonbonded distance. In our geometrical constructions of initial states and transition states we used the normal covalent bond lengths corresponding to the covalent radii in Table 1. However, in the calculation of nonbonded interactions, it is the van der Waals radius of atoms or groups that is the critical distance, and these radii are also given in Table 1; they are taken mainly from the compilations of Pauling [8] and of Bondi.[9] Nonbonded potential functions are available for interactions between like pairs of atoms or groups in the cases H–H,[10] Me–Me,[11] Br–Br,[12] and Hg–Hg.[13] We have slightly adjusted the given functions by the inclusion of constants, α, in the term $(r + \alpha)$ so that the position of the minimum interaction, $r_{min.}$, occurs at the van der Waals distance calculated from the radii in Table 1. For the Cl–Cl and I–I potential functions, we used the Br–Br function, again with adjusted values of $r_{min.}$, and similarly we constructed an Sn–Sn function from the Hg–Hg function.† The various adjusted functions that we have

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† We give in Tables 1—3 data that we shall use in later calculations, as well as data relevant to the present calculations.

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used are in Table 2. In the case of interactions between unlike pairs of atoms or groups, we generally took the arithmetic mean of the two component functions, and

TABLE 1

Covalent bond radii and van der Waals radii, in Å

Atom or group	Covalent radius [a]	van der Waals radius [b]
H	0·32	1·20
C	0·77	
Hg	1·29	1·50
Sn	1·41	1·62 [c]
Cl	0·99	1·75
Br	1·11	1·85
I	1·31	1·96
Me		2·00 [d]

[a] Selected to give the covalent bond distances given in ' Tables of Interatomic Distances and Configurations in Molecules and Ions,' Chemical Society Special Publication No. 11, 1958. [b] Refs. 8 and 9. [c] This value has been chosen to give a difference (van der Waals radius — covalent radius) similar to that for mercury. [d] Also used for groups CH_2, CH, and C when tetrahedrally disposed.

again adjusted them to give the required value of r_{min}. This procedure is not reasonable for unlike functions such

Waals shell of a methyl group as a hemisphere of radius 2 Å attached to a hemiellipsoid of semi-major radius 2 Å and semi-minor radius 1·35 Å (Figure 1). These radii result in there being zero Me–Me interaction in the propane ($MeCH_2Me$) molecule. When the interaction energy, V_r, is calculated for an unlike interaction Me–a,
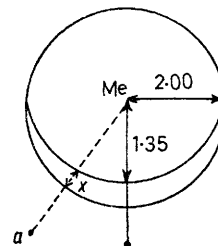

FIGURE 1 The van der Waals shell of a methyl group, and the correction for an Me–a nonbonded interaction

the Me $\cdots a$ distance is calculated normally and then corrected by addition of the distance x in Figure 1 before being substituted in the function $V_r = f(r + \alpha)$; for

TABLE 2

Nonbonded potential functions, $V_r = f(r + \alpha)$, with V_r in kcal mol⁻¹ and r and α in Å

Interaction	V_r	α
H–H	$64 \cdot 5 \left[\left(\dfrac{3 \cdot 06}{r + \alpha} \right)^{12} - 2 \left(\dfrac{3 \cdot 06}{r + \alpha} \right)^{6} \right]$	0·66
Me–Me	$23,050 \left\{ 11,880 \exp \left[-3 \cdot 3295(r + \alpha) \right] - \left(\dfrac{2 \cdot 244}{r + \alpha} \right)^{6} \right\}$	0·205
Hg–Hg	$6756 \cdot 561 \left[\left(\dfrac{2 \cdot 90}{r + \alpha} \right)^{12} - \left(\dfrac{2 \cdot 90}{r + \alpha} \right)^{6} \right]$	0·255
Sn–Sn	As for Hg–Hg	0·015
Cl–Cl	$2146 \cdot 20175 \left[\left(\dfrac{4 \cdot 268}{r + \alpha} \right)^{12} - \left(\dfrac{4 \cdot 268}{r + \alpha} \right)^{6} \right]$	1·29
Br–Br	As for Cl–Cl	1·09
I–I	As for Cl–Cl	0·87

as Me–Hg and Me–Sn because the metal–metal potential functions are much ' harder ' than the nonmetallic functions,* and so we constructed the above two unlike functions by mixing in the ratio 100 : 1, again with the correct values of r_{min}. All the unlike functions are in Table 3.

TABLE 3

Nonbonded potential function for unlike pairs of atoms, with V_r in kcal mol⁻¹ and r and α in Å

a–b	V_r (a–b)		α_a	α_b
H–Me	$\frac{1}{2} V_r$ (H–H)	$+ \frac{1}{2} V_r$ (Me–Me)	1·46	1·005
Me–Cl	$\frac{1}{2} V_r$ (Me–Me)	$+ \frac{1}{2} V_r$ (Cl–Cl)	0·455	1·04
Me–Br	$\frac{1}{2} V_r$ (Me–Me)	$+ \frac{1}{2} V_r$ (Br–Br)	0·355	0·94
Me–I	$\frac{1}{2} V_r$ (Me–Me)	$+ \frac{1}{2} V_r$ (I–I)	0·245	0·83
Me–Hg	V_r (Me–Me)	$+ 0·01 V_r$ (Hg–Hg)	0·705	−0·245
Me–Sn	V_r (Me–Me)	$+ 0·01 V_r$ (Hg–Hg)	0·585	−0·365

Having decided on the nonbonded potential functions, there are still a number of factors to take into account. First, the van der Waals shell of a methyl group cannot be regarded as spherically symmetrical, since the three hydrogen shells project mainly in the direction away from the methyl bond. We therefore took the van der

* By ' harder ' we mean that the repulsive energy increases more rapidly as the internuclear distance is decreased.

Me–Me interactions, two such corrections must be made. Secondly, if two nonbonded groups a and b are jointly attached to a third atom (Figure 2), the a–b interaction will be reduced because of shielding by the intervening atom. The shielding will depend on the angle ω and we have in all cases (including interactions when a or b are
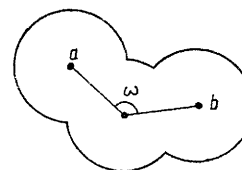

FIGURE 2 The angle ω in a three atom system

methyl groups) applied a factor to incorporate the effect of this shielding in the term $E = V_r \cos (\omega/2)$, where V_r is the nonbonded interaction calculated from $V_r = f(r + \alpha)$, and E is the interaction corrected for shielding. When the groups a and b are connected through two intervening atoms, a similar correction is applied, but now ω refers to the torsion angle as shown in Figure 3.

Using the above methods, it is possible to calculate the

direct nonbonding interactions in the transition states and also in the initial states. We find that such interactions involving hydrogen atoms are so small that they can be ignored. Hence we can take the initial state CH_3HgBr and the transition state $[CH_3HgBr\!\!:\!\!HgBr_2]^{\ddagger}$ as standards, and calculate the additional interactions in both initial state (E^i) and transition state $(E^{\ddagger})$ that arise when various alkyl substituents are introduced. Although we shall deal only with essentially rigid models, rotation of groups is allowed as usual, and it is therefore necessary to find the energy minima $(E^i_{min.}$ and $E^{\ddagger}_{min.})$ as different substituents are introduced.* The rate factor corresponding to these energy minima will then be given by $\exp[-(E^{\ddagger}_{min.} - E^i_{min.})/RT]$.

However, even in the simplest case of one additional α-Me group (as in $MeCH_2HgBr$) there are rotational restrictions in the transition state to take into account. Consider a transition state such as that in Figure 4. The three atoms Hg, C, and Hg define an isosceles triangle
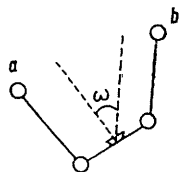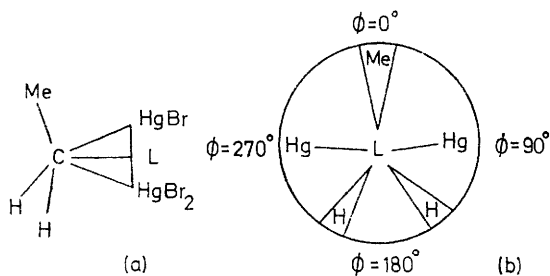

FIGURE 3 The angle ω in a four atom system

FIGURE 4 Two views of the transition state, illustrating α-rotation

with each C–Hg bond the same length, and the two Hg $\cdots$ L distances are also equal. Then the three substituent atoms (H, H, Me) attached to C are each arranged so that the tetrahedral angles $\widehat{HCL}$ and $\widehat{MeCL}$ are preserved. Although the model is essentially rigid, the groups H, H, and Me are able to rotate about the C–L axis as shown in Figure 4b. Rotation of the methyl group about the C–L axis is, however, not free because the methyl group can eclipse a mercury atom or can adopt the staggered arrangement of Figure 4b. Since the geometry is well defined, the nonbonded interactions can all be calculated as a function of the angle of rotation ϕ to give a rotational energy profile (Figure 5). We then calculate the effect of such rotational restriction on the reaction rate constant as follows. The potential well is fitted to a parabolic function of type $E = \frac{1}{2}Kq^2$ where K

* Both $E^i_{min.}$ and $E^{\ddagger}_{min.}$ can take positive and negative values; the positive values arise because of the repulsive part of the non-bonded potential functions, and the negative values because of the attractive part.

is a force constant and q is the distance moved from the potential minimum. The energy levels for such a motion are given by $E_n = (h/2\pi)(K/m)^{\frac{1}{2}}(n + \frac{1}{2})$ where h is
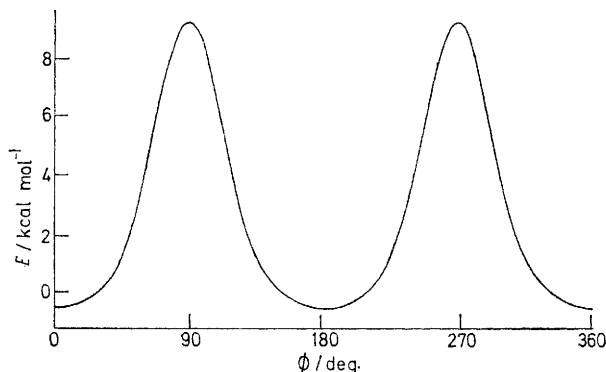

FIGURE 5 The α-rotational energy profile for the ethyl transition state (cf. Figure 4)

Planck's constant, m is the mass of the rotating group, and n is an integer. The population proportion in any level (N_n) can be calculated from the Boltzmann distribution, with respect to the total population $(\Sigma_1^{\infty} N_n)$ as unity. The angle over which the population in any level is able to rotate $(\Delta\phi_n)$ can be found from the rotational profile, and the average rotational angle then calculated as $\Sigma_1^{\infty} N_n . \Delta\phi_n$. For completely free rotation the rotational angle is 360° and the rotational factor influencing the rate is given by $(\Sigma_1^{\infty} N_n . \Delta\phi_n)/360$; naturally, the population above the energy barrier is taken into account, so that for that fraction of molecules, $\Delta\phi_n = 360$. For α-methyl substituents there is free rotation in the initial state (e.g. for $MeCH_2HgBr$) since the Me–Hg and Me–Br interactions are constant, and an α-rotational restriction in the transition state (see Figure 4). For β-methyl substituents there is restricted rotation in the initial state (F^i_β) and a β-rotational restriction in the transition state $(F^{\ddagger}_\beta)$ (Figure 6), as well as an α-rotational restriction
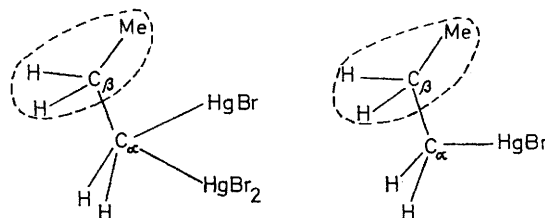

FIGURE 6 Transition state and initial state β-rotation in the $MeCH_2CH_2$ group

in the transition state $(F^{\ddagger}_\alpha)$. We have not attempted to ' couple ' the α- and β-rotations in the transition state, but have treated them as two independent rotations. For example, with R $= MeCH_2CH_2$, we calculate the α-rotation due to the group $MeCH_2$, rotating about the C–L axis (Figure 4). Then, with the CH_2 group placed at its position of minimum energy (in this case with $\phi = 0$, Figure 4), the β-rotational profile is constructed as the Me group rotates about the C_α–C_β axis as in Figure 6; here again there are positions of maximum interaction as

the rotating methyl group eclipses the two mercury atoms in the transition state. In the case of initial state β-rotation, the situation is simpler and there is only one rotational profile to consider. Note that in all the above cases, when more than one methyl group is rotating (as in the transition state α-rotation for Me_2CH or in β-rotations for Me_2CHCH_2), interactions involving all the rotating methyl groups must be summed to yield the final α- or β-rotational profile.

The overall rotational factor is given by $F = F^{\ddagger}_{\alpha} \cdot F^{\ddagger}_{\beta}/F^{i}_{\beta}$, with $F^{\ddagger}_{\beta}$ and F^{i}_{β} taken as unity for the α-methylated series of alkyl groups. The final expression for the rate factors k^R/k^{Me} is then given by equation (2).

$$k^R/k^{Me} = F \cdot E$$
$$= \frac{F^{\ddagger}_{\alpha}F^{\ddagger}_{\beta}}{F^{i}_{\beta}} \exp\left[-(E^{\ddagger}_{min.} - E^{i}_{min.})/RT\right] \qquad (2)$$

The transition state rotational factor $F^{\ddagger}_{\alpha}F^{\ddagger}_{\beta}$ may be regarded as a measure of the decrease in entropy of the transition state. The total rotational factor $F = F^{\ddagger}_{\alpha}F^{\ddagger}_{\beta}/F^{i}_{\beta}$ then influences the reaction rate constant through an activation entropy effect that is numerically equal to $\delta\Delta S^{\ddagger} = R \ln F$. When F is less than unity (as is usually the case) the activation entropy will be more negative in comparison to the value of $\Delta S^{\ddagger}$ for the standard methyl compound. Alternatively, the term $F^{\ddagger}_{\alpha}F^{\ddagger}_{\beta}$ may be viewed as a measure of the possible configurations of the transition state, again by comparison to the methyl compound; the total factor F then represents the proportion of available pathways from reactants to transition state in comparison to the number available for the standard methyl compound.

RESULTS AND DISCUSSION

The experimental observation on reaction (1) may be summed up as follows. Reaction 1 ($R = Bu^s$, $X = OAc$) has been shown to proceed with retention of configuration at the carbon atom undergoing substitution,[14] and is accelerated by addition of inert salts such as lithium nitrate and by addition of a more polar solvent, water.[14] An open transition state was therefore suggested by Ingold and his co-workers.[14] Hughes and Volger[2] later investigated the effect of changing the alkyl group, R; the relative rate constants they obtained are R = Me (1), Et (0·42), and Bu^tCH_2 (0·33) for X = Br at 100°, and R = Me (1) and Bu^s (0·062) for X = OAc at 60°. We have carried out calculations for the case of X = Br both at 60° and 100°, reasoning that the change from X = Br to X = OAc would effect the relative rate constant only marginally.

The transition state model that we have adopted corresponds closely to the open transition state of Hughes and Volger; the fixed dimensions are given in Figure 7. We left the C · · · Hg partial bond length and the $\widehat{HgCHg}$ angle, ψ, as variable parameters, noting that the angle suggested by Hughes and Volger (81°) is very close

to that calculated by Gielen and Nasielski (76·8°).[15] The entering $HgBr_2$ group is almost entirely free to rotate about the C_{α} · · · Hg axis in such a way that Me–Br interactions between α-Me (or β-Me) groups and the bromine atoms are extremely small. Similarly, such Me–Br interactions involving the leaving Br atom are also very
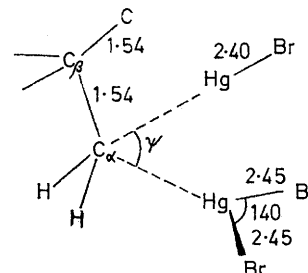

FIGURE 7 Bond lengths (Å) and angles (deg.) in the open transition state

small, and the main direct interactions in the transition state are the Me–Hg ones.

We carried out a preliminary survey of calculated relative rates, using equation (2), as ψ was varied from 76·8 to 89·0° and the C · · · Hg partial bond lengths from 2·25 to 2·35 Å. The final calculated relative rates are in Table 4, and show that (i) steric effects increase as the

TABLE 4

Variation of calculated rate constants [a] with dimensions of the open transition state

$\widehat{HgCHg}$ Angle (ψ) (°)	C · · · Hg Length (Å)	Et ($T = 100°$)	Bu^tCH_2 ($T = 100°$)	Bu^s ($T = 60°$)
76·8	2·25	0·53	0·36	0·09
	2·30	0·56	0·48	0·12
	2·35	0·59	0·63	0·16
81·0	2·25	0·49	0·33	0·06
	2·30	0·52	0·43	0·08
	2·35	0·55	0·56	0·11
85·0	2·25	0·46	0·30	0·04
	2·30	0·49	0·39	0·05
	2·35	0·51	0·50	0·07
89·0	2·25	0·43	0·29	0·02
	2·30	0·46	0·37	0·03
	2·35	0·48	0·47	0·05
Observed relative rate constants [a]		0·42	0·33	0·06

[a] Rate constants are relative to $k^{Me} = 1$.

angle ψ is increased, (ii) steric effects decrease as the partial bond lengths are increased, and (iii) there is substantial agreement between calculated and observed relative rates for a number of combinations shown in Table 4. We then carried out calculations for the complete range of alkyl groups with ψ fixed at 84° and the C · · · Hg length at 2·288 Å; results are in Table 5. Calculated and observed rates are in excellent agreement, and the general trend of relative rates predicted is clearly reasonable.[*]

A breakdown of the calculated relative rates into E

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* The value for R = Bu^t may well be too low, since it is not reasonable to expect an essentially rigid model to yield reliable results for very hindered systems.

[14] E. D. Hughes, C. K. Ingold, F. G. Thorpe, and H. C. Volger, J. Chem. Soc., 1961, 1133.

[15] M. Gielen and J. Nasielski, Ind. chim. belge, 1961, 26, 1393.

and F factors is given in Table 6. It is interesting that (except for R $=$ Bu^t) the major contributing factor is always that of rotational restriction in the transition state; in many cases, the direct effect E would by itself lead to an increase in rate for the higher alkyls. This is because α-Me and β-Me groups in the transition state can very often rotate until they are close to the Me–Hg van

contributions between the three bromine atoms (Figure 8) and the α-Me and β-Me groups in the transition state.

In conclusion, our calculations are not in accord with a cyclic transition state (Figure 8), but are commensurate with an open transition state (Figure 7) in which $\psi = 84°$ and the C $\cdots$ Hg partial bond lengths are 2·288 Å. Excellent agreement with the observed relative rates is

TABLE 5

Calculated relative rate constants ^{a} for the open transition state, with $\psi = 84°$ and C $\cdots$ Hg $= 2·288$ Å

		Et	Pr^n	Bu^i	Bu^{t}CH$_2$	Pr^i	Bu^s	Bu^t
$T = 60°$	Calc.	0·515	0·461	0·413	0·387	0·068	0·049	2 × 10^{-6}
	Obs.						0·062	
$T = 100°$	Calc.	0·502	0·451	0·405	0·377	0·076	0·056	9 × 10^{-6}
	Obs	0·42			0·33			

^{a} Rate constants are relative to $k^{Me} = 1$.

TABLE 6

The direct enthalpic factors (E) and rotational factors (F) in initial states and open transition states ($\psi = 84°$ and C $\cdots$ Hg $= 2·288$ Å)

	Et	Pr^n	Bu^i	Bu^{t}CH$_2$	Pr^i	Bu^s	Bu^t
$E^i{}_{min.}$	-182	-436	-624	-624	-364	-618	-545
$E^{\ddagger}{}_{min.}$	-392	-682	-939	-914	$+205$	-133	$+7528$
$E^{\ddagger}{}_{min.} - E^i{}_{min.}$	-210	-246	-315	-290	569	485	8065
At 60°							
$F^i{}_\beta$	(1)	0·734	0·616	0·560	(1)	0·734	(1)
$F^{\ddagger}{}_\alpha$	0·375	0·375	0·375	0·375	0·161	0·161	0·433
$F^{\ddagger}{}_\beta$	(1)	0·623	0·422	0·373	(1)	0·470	(1)
$F = F^{\ddagger}{}_\alpha F^{\ddagger}{}_\beta / F^i{}_\beta$	0·375	0·318	0·257	0·250	0·161	0·103	0·433
E	1·373	1·450	1·609	1·550	0·423	0·481	5·1 × 10^{-6}
$F . E$	0·515	0·461	0·413	0·387	0·068	0·049	2·2 × 10^{-6}
At 100°							
$F^i{}_\beta$	(1)	0·753	0·641	0·586	(1)	0·753	(1)
$F^{\ddagger}{}_\alpha$	0·378	0·378	0·378	0·378	0·164	0·164	0·457
$F^{\ddagger}{}_\beta$	(1)	0·645	0·449	0·396	(1)	0·495	(1)
$F = F^{\ddagger}{}_\alpha F^{\ddagger}{}_\beta / F^i{}_\beta$	0·378	0·324	0·265	0·255	0·164	0·108	0·457
E	1·327	1·393	1·529	1·478	0·464	0·520	1·9 × 10^{-5}
$F . E$	0·502	0·451	0·405	0·377	0·076	0·056	8·7 × 10^{-6}

der Waals distance of 3·50 Å, where they experience a net methyl-to-mercury attraction. With $\psi = 84°$ and the C $\cdots$ Hg partial bonds fixed at 2·288 Å, the Hg–Hg distance in the transition state is 3·06 Å; this is very close to the Hg–Hg van der Waals distance of 3·0 Å (Table 1), and corresponds to an attraction of 1·67 kcal mol^{-1}.

Although the experimental observations [14] indicate an open transition state in reaction (1), it is not easy to differentiate between open and cyclic transition states in S_E2 reactions that proceed with retention of configuration. We therefore carried out another preliminary survey of calculated relative rates, but this time based on the cyclic model (Figure 8). Results are in Table 7, and show that no matter what are the values of ψ and the C $\cdots$ Hg partial bond lengths (with ψ varied from 76·8 to 89°, and C $\cdots$ Hg from 2·15 to 2·35 Å), there is little agreement between the calculated and observed relative rate constants. In particular, all the calculated relative rates for R $=$ Et, Bu^{t}CH$_2$, and Bu^s are far too high, with those for Bu^{t}CH$_2$ being much larger than unity. Without giving the complete breakdown of relative rates into the terms E and F, it can be said that the very high calculated relative rates arise because of large attractive

obtained, purely on the basis of steric effects in initial and transition states. It is noteworthy that no polar

TABLE 7

Variation of calculated rate constants ^{a} with dimensions of the cyclic transition state

$Hg\widehat{C}Hg$ Angle (ψ) (°)	C $\cdots$ Hg Length (Å)	k^R/k^{Me} Et ($T = 100°$)	k^R/k^{Me} Bu^{t}CH$_2$ ($T = 100°$)	k^R/k^{Me} Bu^s ($T = 60°$)
76·8	2·15	0·71	2·11	0·26
	2·25	0·79	3·37	0·49
	2·35	0·86	5·57	0·84
81·0	2·15	0·65	1·94	0·15
	2·25	0·72	3·28	0·32
	2·35	0·79	4·97	0·58
85·0	2·15	0·60	1·82	0·19
	2·25	0·67	3·03	0·20
	2·35	0·73	4·55	0·39
89·0	2·15	0·56	1·71	0·12
	2·25	0·62	2·82	0·26
	2·35	0·68	4·22	0·25
Observed relative rate constants ^{a}		0·42	0·33	0·06

^{a} Rate constants are relative to $k^{Me} = 1$.

contributions of the alkyl groups undergoing substitution have to be assumed.

In all our calculations we have assumed essentially rigid models for the transition states, with no allowance for bond bending or bond stretching. Although such
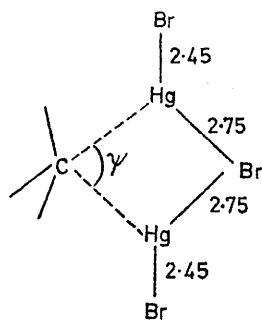

FIGURE 8   Bond lengths (Å) in the cyclic transition state

models are only of limited application, they are clearly useful when steric effects are rather small, and when there is therefore comparatively little steric relief to be gained by bond bending or stretching. The advantage of such simple models is that they enable the number of variable parameters to be kept to a minimum. For example, once the nonbonded potential functions have been fixed, the calculations on the open transition state model are then carried out using only two variable parameters (ψ and the C $\cdots$ Hg partial bond length).*

* And even these parameters are kept constant within a given series.