Approximate source pressures were measured by inserting, in place of the solids probe, a probe consisting of a calibrated thermocouple gauge on a 25-cm length of stainless steel tubing with a Teflon end machined to fit the source opening for the solids probe. The thermocouple gauge was separately calibrated with both H_2 and CH_4 against a capacitance micromanometer. This arrangement permitted establishment of the (approximately linear) relation between the reagent gas pressure behind the reagent gas inlet leak and the source pressure. This was used to estimate source pressures when the solids probe was used.

All samples used were commercially available except 7-methoxy-cycloheptatriene which was prepared by the reaction of tropylium tetrafluoroborate with sodium methoxide.[16]

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Steric Effects in S_N2 Reactions

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Abstract: Steric effects for S_N2 reactions of the classical alkyl series have been calculated by molecular mechanics using full relaxation and a force field based on reasonable estimates for the several special constants required. The results show appreciable differences from earlier calculations based on static models and questionably weak nonbonded functions. As expected, agreement is good for the β series (Et, n-Pr, i-Bu, neo-Pe) for a modest range of variations in the force field constants, and the observed relative rates can be explained wholly from steric effects. Formal requirements which justify the equating of ΔH values with steric energy differences are not properly met in the α series, and in fact agreement between calculated and observed rates is poor for this series (Me, Et, i-Pr, t-Bu). Thus methyl halides are reported to react 60 times faster than ethyl bromide while steric effects predict the much larger factor of 35 000. *tert*-Butyl bromide, on the other hand, has such a high steric interference in the S_N2 transition state that the C_α-$Br^{1/2}$ bonds are greatly elongated. Even so the predicted rate is much smaller than the observed rate. Whether such a reaction is to be classified as S_N2 or something else, it needs a large accelerating polar factor to overcome the steric hindrance. Steric hindrance in the transition state is relieved in part by bending the $Br^{-1/2}$-C_α-$Br^{-1/2}$ bond in primary and secondary systems. With complete relaxation the total strain becomes distributed throughout the molecule. Although the relative degree of strain is ultimately due to H···Br and C···Br nonbonded contacts, the transition state models do not show unusually short contacts; nor is there any simple parallel with total hindrance. The shortest H···Br distance found in the classical alkyl series is in Br-i-Bu-Br where the α-H eclipses one bromine atom and is only 2.4 Å distant. Experimental data for the classical alkyl series have been reevaluated to provide a suitable data set for comparison with calculated steric energies. The molecular mechanics computations have utilized transition state models which either directly or indirectly force the two C_α-Br distances to remain equal and other models which do not force quasi-symmetry. Since the quasi-symmetric models have the higher energies, our force field treats them as transition states rather than stable complexes.

Introduction

Substitution reactions are subject to steric retardation and acceleration.[1-3] Detailed studies by Schleyer's group based on molecular mechanics have provided a good account of steric effects in the solvolysis reaction.[3-6] Much less is known about steric effects in S_N2 substitution despite the fact that it is one of the first reactions to be treated theoretically.[1] In an important pioneering study Ingold's group performed hand calculations on models of the transition state (Figure 1). To make the task manageable they adopted a single appropriate rigid conformation for the transition state for each alkyl group and calculated the H···Br nonbonded distances. For all shorter than the expected van der Waals contact distance they calculated the repulsive energy. The sum of these repulsive energies was taken as the steric energy; the starting alkyl halides were assumed to be strain free. The study included the classical series of alkyl groups: methyl, ethyl, n-propyl, isobutyl, neopentyl, isopropyl, and *tert*-butyl. It proved necessary to allow the C_α···Br semibond distances to vary, or else *tert*-butyl was out of line with other groups. Remarkably enough this primitive model gave a reasonably quantitative account of the relative rates.

In a series of papers published some years later the calculations were refined and the experimental base was greatly expanded.[7-15] The classical alkyl series was treated, but in greater detail. In the extended model the Br···C_α···Br axis was allowed to bend as well as stretch and entropy effects were treated in detail.[15]

A more recent study has examined both front-side and back-side attack using simplified stiff models and grouped interactions.[16]

Further progress would be facilitated by improved theoretical treatment of representative systems. Results to date are somewhat discordant. INDO and CNDO calculations on $(F-CH_3-F)^-$ show a C–F bond length 8% longer than for CH_3F.[17,18] Ab initio calculations show a 35, a 32, or a 27% longer bond.[19a,b,20] The ab initio calculations show a 34% larger bond in $(Cl-CF_3-Cl)^-$. There is lack of agreement on whether the complex is stable, but stabilization energy is in any event low.

A correlation of x-ray results on cadmium complexes with distorted trigonal bipyramid geometries has provided what appears to be a general relationship among bond changes for this atomic geometry.[21] If for the S_N2 reaction we use the C–C bond length to calculate the maximum displacement of the C_α carbon atom in reaching the transition state (0.51 Å), then Bürgi's eq 3 predicts an elongation of 0.31 Å, a 16% change for C–Br or for C–Cl.

These various estimates may lack somewhat in precision, but all are within a relatively narrow range. Older estimates based on approximate molecular properties gave similar results. Ingold's group used 25% elongation for CH_3Br in 1946 and 16% in 1955.[1,15]

High-pressure mass spectrometry has permitted observation of ions $(RX_2)^-$ in the gas phase.[22,23] The enthalpies follow the usual pattern of increasing stability of complex with increasing size of alkyl group, R = neopentyl being the most stable ion of the classical series. Ion cyclotron resonance studies of S_N2 reactions in the gas phase show a relatively small steric effect.[24] This behavior and other reaction features have been explained on the basis of a so-called double potential well. In the gas phase the nuclophiles and the substrates form a reactant complex which is subsequently transformed to a product complex. Overall rates depend on both reaction steps.

In the present study we have applied the methods of molecular mechanics to the classical alkyl series. It is possible to set reasonable limits on the constants adopted in the force field. Applications to more extensive series of reactants may be expected to further narrow these limits and to increase our understanding of steric effects.

Reevaluation of Experimental Data

The calculated steric energies are to correlate relative reaction rates or other thermodynamic quantities. Since summaries of the data contain appreciable discrepancies and are incomplete, we have subjected most of the available data to a least-squares evaluation of both the Arrhenius and transition state parameters. Results are summarized in Table 1.

There are always uncertainties in piecing together rates measured in various laboratories, but there are technical difficulties endemic to the exchange reactions that pretty much restrict useful comparisons to whatever compounds were included in a given study. For example, exchange reactions are reversible, but the calculations have usually applied ordinary kinetic expressions to early reaction stages. In a few reactions salt precipitation caused some difficulty. Many of the reactions show huge changes in rate constants on going from highly dilute solution up to 0.1 M salt. This sensitivity is due in part to incomplete dissociation of the salts; the ion pairs and higher clusters are relatively inert.[14,25-29] Conventional salt effects are also present. These various complications make it unlikely that rate constants obtained in one laboratory could be duplicated elsewhere since important details tend to be lacking.

The data in Table 1 are adequate for comparing relative rates among alkyl groups. The original references should be consulted, however, before any attempt is made to compare other relative reactivities such as between chloride ion and bromide ion. As one example, the difference between apparent k_2 values for chloride ion based on the stoichiometric lithium
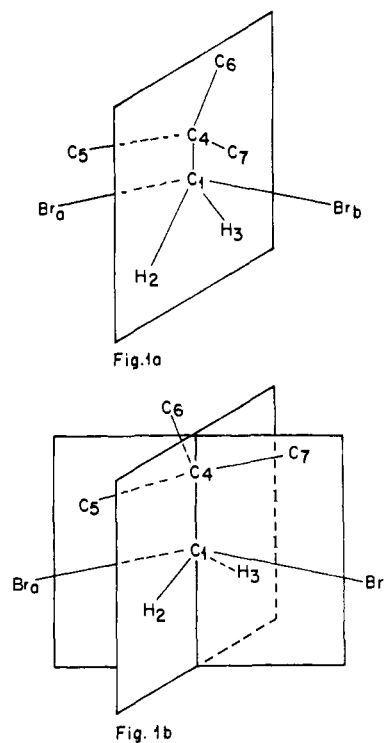

Fig. 1a

Fig. 1b

Figure 1. (a) C_s symmetry; atoms H_2, H_3, C_1, C_4, and C_6 lie in the mirror plane. (b) C_s symmetry; atoms Br_a, Br_b, C_1, C_4, and C_7 lie in the mirror plane.

chloride concentrations and the corrected rate constants based on the concentration of free chloride ion may differ by a factor of several hundred.[25,27,29]

In order to evaluate the significance of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values it is necessary to have error limits. These depend jointly on the spread of the temperatures used (that is, on the reciprocal matrix of the normal equations) and on the error estimate for the rate constants themselves. We base the latter on the difference between observed rate constants and those calculated from the Arrhenius equations; this is 7% (300 df). The data seem to be of comparable accuracy, apart from a few sets where purported experimental values were apparently derived from the Arrhenius expression. We report standard deviations for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. If necessary these could be converted to confidence limits by standard procedures.

It would clearly be of interest to sort out the separate contributions of polar effects and steric effects on the enthalpy and the entropy of activation. Regrettably the available data do not support such a dissection. Figure 2 shows plots of $\Delta S^{\ddagger}$ observed vs. calculated. Figure 2a is based on the Ingold calculation of $\Delta S^{\ddagger}$. We show data for two typical exchange reactions in acetone. While the data fit lines within experimental accuracy, the slopes are variable and range from small to appreciably larger than one. The $\Delta S^{\ddagger}$ values calculated by Abraham (Figure 2b) give a poorer correlation with experimental $\Delta S^{\ddagger}$.[17]

There is some reason to believe that the fit is fortuitous. The $\Delta S^{\ddagger}$ for the LiCl + RBr reaction in dimethylformamide show only a scatter plot. In fact, the χ^2 test at the 90% level shows that these $\Delta S^{\ddagger}$ values may be considered constant for all seven alkyl groups. Whatever the correct assessment of the gas-phase entropy values may be, they are apparently swamped by large entropies of solvation. On the grounds that the solvation effects might be volume dependent, we have plotted observed $\Delta S^{\ddagger}$ against the molecular weight of the alkyl group, Figure 2c. This hypothesis gives as good a correlation as does the Ingold treatment.

Table I. Summary of Rate Data

Alkyl group	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger a}$	$k(25\ °C)^b$	$\ln k\ (\text{obsd})^b$	$\ln k\ (\text{calcd})^c$
		RBr + LiBr (Acetone)[10]	$a = -6.3099$	$b = -1.6521$	
Me	15.476 ± 0.8	-10.588 ± 3.3	$1.36 -1$	-1.995	-2.318
Et	17.038 ± 0.5	-14.143 ± 1.7	$1.65 -3$	-6.407	-6.310
n-Pr	16.890 ± 0.7	-15.443 ± 2.5	$1.10 -3$	-6.812	-6.768
i-Bu	18.554 ± 0.6	-15.685 ± 2.0	$5.88 -5$	-9.741	-9.598
neo-Pe	21.024 ± 0.7	-22.450 ± 1.8	$2.93 -8$	-17.346	-17.346
i-Pr	19.247 ± 0.8	-15.777 ± 2.3	$1.74 -5$	-10.959	-10.643
t-Bu			$5.2\ \ -6$	-12.17^d	-12.93
		RBr + LiCl (Acetone)[8]	$a = -8.9166$	$b = -1.5465$	
Me	15.194 ± 0.5	-17.785 ± 1.6	$5.93 -3$	-5.128	-5.180
Et	16.838 ± 0.4	-20.436 ± 1.4	$9.75 -5$	-9.236	-8.917
n-Pr	17.133 ± 0.4	-20.260 ± 1.4	$6.49 -5$	-9.643	-9.345
i-Bu	18.221 ± 0.6	-19.500 ± 1.9	$1.51 -5$	-11.101	-11.995
neo-Pe	20.637 ± 1.0	-28.371 ± 2.5	$2.85 -9$	-19.676	-19.508
i-Pr	17.800 ± 0.4	-24.948 ± 1.3	$1.98 -6$	-13.132	-12.973
t-Bu			$3.1\ \ -7$	-14.98^d	-15.12
		RBr + Et₄NCl (Dimethylformamide)[25]	$a = -4.5872$	$b = (-1.6878)^e$	
Me	17.694 ± 0.4	-8.045 ± 1.4	$4.46 -1$	-0.807	-0.509
Et	18.524 ± 0.5	-5.394 ± 1.6	$1.10 -2$	-4.512	-4.587
n-Pr	17.363 ± 0.5	-10.348 ± 1.6	$6.44 -3$	-5.046	-5.055
i-Bu	18.753 ± 0.4	-11.375 ± 1.2	$3.67 -4$	-7.910	-7.947
neo-Pe	25.506 ± 0.5	-5.644 ± 1.4	$7.22 -8$	-16.444	-16.146
i-Pr	20.580 ± 0.4	-6.500 ± 1.2	$1.96 -4$	-8.539	-9.014
t-Bu	20.169 ± 0.5	-13.485 ± 1.5	$1.17 -5$	-11.356^f	
		RBr + LiI (Acetone)[11]	$a = -6.0960$	$b = -1.6981$	
Me	16.090 ± 0.6	-7.137 ± 2.2	$2.76 -1$	-1.286	-1.993
Et	18.490 ± 0.9	-9.268 ± 3.6	$1.66 -3$	-6.401	-6.096
n-Pr	19.018 ± 0.8	-7.855 ± 2.7	$1.38 -3$	-6.584	-6.566
i-Bu	19.656 ± 0.9	-11.974 ± 2.8	$5.92 -5$	-9.735	-9.476
neo-Pe	23.531 ± 0.7	-13.632 ± 1.9	$3.67 -8$	-17.120	-17.725
i-Pr	20.001 ± 1.0	-13.888 ± 2.8	$1.26 -5$	-11.281	-10.550
		RI + LiCl (Acetone)[9]	$a = -8.1500$	$b = -1.4892$	
Me	15.302 ± 0.3	-17.956 ± 1.1	$4.54 -3$	-5.395	-4.552
Et	16.557 ± 0.6	-18.470 ± 1.8	$4.22 -4$	-7.771	-8.150
n-Pr	16.608 ± 0.4	-19.166 ± 1.3	$2.41 -4$	-8.331	-8.563
i-Bu	17.537 ± 0.5	-21.721 ± 1.4	$1.57 -5$	-11.062	-11.114
neo-Pe	21.278 ± 0.7	-24.868 ± 1.7	$5.71 -9$	-18.981	-18.348
i-Pr	17.195 ± 0.5	-23.223 ± 1.4	$1.31 -5$	-11.243	-12.056
		RI + LiBr (Acetone)[12]	$a = -4.2977$	$b = -1.4988$	
Me	15.645 ± 0.5	-7.493 ± 1.9	$4.91 -1$	-0.711	-0.674
Et	16.953 ± 0.7	-10.069 ± 2.4	$1.48 -2$	-4.213	-4.298
n-Pr	17.533 ± 0.4	-8.840 ± 1.2	$1.03 -2$	-4.576	-4.713
i-Bu	17.140 ± 0.7	-16.650 ± 2.0	$3.89 -4$	-7.847	-7.283
i-Pr	17.676 ± 0.7	-14.856 ± 2.0	$3.91 -4$	-7.852	-8.231
t-Bu			$1.0\ \ -6$	-13.82^d	-12.90
		RI + LiI (Acetone)[13]	$a = -2.9880$	$b = -1.5577$	
Et	16.888 ± 0.6	-7.381 ± 2.3	$6.32 -2$	-2.762	-2.988
neo-Pe	20.461 ± 0.7	-16.791 ± 2.1	$1.35 -6$	-13.515	-13.656
i-Pr	18.759 ± 0.6	-10.428 ± 2.3	$5.87 -4$	-7.441	-7.074
t-Bu			$1.8\ \ -4$	-8.62^d	-9.23
		NaOEt (EtOH)[1]	$a = -0.614$	$b = -1.672$	
Me			17.6	2.868	3.416
Et			$1.$	$0.$	-0.614
n-Pr			$2.8 -1$	-1.273	-1.083
i-Bu			$3.0 -2$	-3.507	-3.942
neo-Pe			$4.2 -6$	-12.380	-12.069

[a] $\Delta H^{\ddagger}$ in kcal mol⁻¹, $\Delta S^{\ddagger}$ in cal deg⁻¹ mol⁻¹ may be used to calculate k at other temperatures. [b] From Arrhenius equation, s⁻¹ M⁻¹. [c] From eq 2 using the a and b values shown with E_i from Table II. Standard deviation of $\ln k$ 0.55 (or 0.24 in log k), 19 df; standard deviation of a values 0.3. Standard deviation of b values 0.1. Average of seven b values 1.590 ± 0.1. [d] $E_{t\text{-}Bu}$ not based on this value. [e] Defined to be $1000/(298R)$. [f] $E_{t\text{-}Bu}$ based solely on this value.

Plots of $\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$ give straight lines within experimental accuracy for all the data; we are therefore justified in using relative rate data for comparison with theory. In fact the interpolated or extrapolated rate constants at 25 °C or at, say, 60 °C represent the most accurate available summary of the rate data.[30] These are clearly superior to the particular $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ observed for some one reaction. Equation 1 summarizes the relationships, $m_{\Delta s}$ being the slopes of the $\Delta H^{\ddagger} - \Delta S^{\ddagger}$ lines

Table II. Observed and Calculated $\Delta\Delta H^{\ddagger}$

Alkyl group	E_i(exptl)[a]	$\Delta\Delta SE_i$[b]	Log k_{rel}[c]	Log k_{rel}[d]
Me	−2.42	−6.20	−1.77	−1.5
Et	0.	0.	0.	0.
n-Pr	0.28	0.04	0.20	0.4
i-Bu	1.99	1.87	1.46	1.5
neo-Pe	6.85[e]	7.03	5.02	5.0
i-Pr	2.62	4.61	1.92	1.6
t-Bu	4.01[f] (5.6)[g]	11.77	2.94 (4.1)	

[a] Effectively $\Delta H_i{}^{\ddagger} - \Delta H^{\ddagger}{}_{ethyl}$; see text. Standard deviation 0.2. [b] Calculated $\Delta H_i{}^{\ddagger} - \Delta H^{\ddagger}{}_{ethyl}$. See Table IV. [c] $1000E_i/(298\cdot2.3R)$ $= 0.733E_i$. [d] Reference 30, p 585. [e] Standard deviation 0.4. [f] This value is uncertain. See text. [g] Average based on the *t*-Bu data in Table I flagged with a *d* footnote. $E = (\ln k - \ln 15 - a_j)/b_j$ assuming that substitution is $^1/_{15}$ of total rate and elimination is the rest.

and $b_{\Delta s}$ the intercept. The intercept term drops out when relative rates are compared.

$$RT \ln k = \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$
$$= \Delta H^{\ddagger}(1 - Tm_{\Delta s}) + b_{\Delta s}T \quad (1)$$

It has been known that relative S_N2 rate constants for a given pair of alkyl groups are more or less independent of the reaction system.[1,30] A common way of summarizing the data is by simple averaging. We have chosen instead the more general averaging technique based on the linear free energy equation

$$\ln k_{ij} = a_j + b_jE_i \quad (2)$$

For each alkyl group we postulate an energy term E_i which is to equal $g\Delta G^{\ddagger}$, and to be so chosen as to make the proportionality constant g nearly equal to one. For each reaction there is an intercept $a_j = \ln k_{ref}$ and a slope, b_j. We define two reference values: $E_{ethyl} = 0$ and $b = -1000/RT$ for the reaction RBr + LiCl in dimethylformamide. Best values of the a_j, b_j, and E_i were found by simultaneous least-squares adjustment of all parameters. The results are summarized in Table II as E_i (exptl) while the a_j and b_j are listed in Table I for each reaction.

The average values of the slopes, $b_{av} = 1.59 \pm 0.1$, are consistent within the 0.1 estimated standard deviation of b based on the least-squares adjustment. Hence the choice of reference b is relatively unimportant since for all reactions $b_j = b_{av}$ within the error limits. The log k_{rel} values are also presented in Table II and these compare closely with rough approximations summarized by Streitwieser.[30]

The E_i values may be considered as defining the effect of a given alkyl group on the rate of an S_N2 reaction. The standard deviation of the calculated $\ln k$ values in Table I is 0.55 with 19 df; in other words, given the a_j and b_j for a given reaction, the calculated rate constant for a given alkyl group is within 50% of the observed value. Examination of the error patterns suggests that about half of the error, perhaps more, arises from systematic procedural variations. Insofar as kinetic measurements are performed on one halide at a time there arise many chances for uncontrolled variables to affect relative rates; examples might include changes of reagents, changes of solvents, or changes of operating techniques.

The entries for the sodium ethoxide data show that relative rates for this reaction are also summarized by the E_i. Data are not available for other charge types.

We consider next the status of S_N2 reactions for *tert*-butyl halides. Winstein et al.[31] present arguments that the observed rates may not be measuring the S_N2 reaction. They report a yield of $3 \pm 1\%$ for *t*-BuCl in the reaction *t*-BuBr + LiCl in acetone. Most of the reaction is an elimination to form isobu-
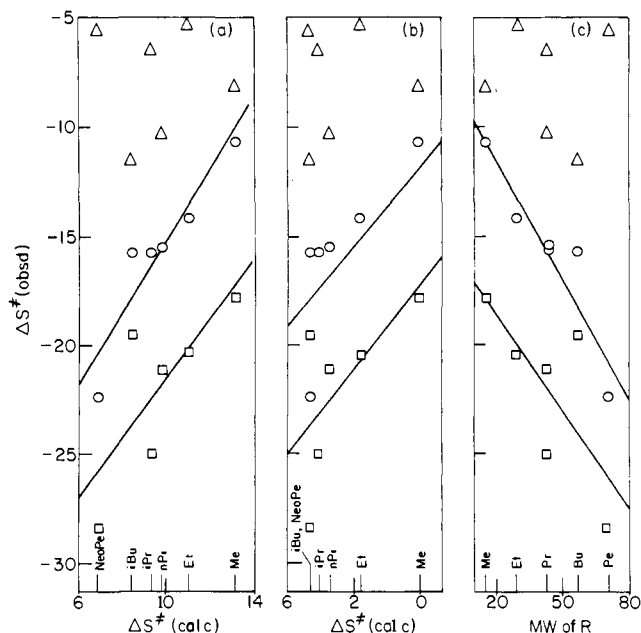

Figure 2. Δ for Et_4NCl + RBr in DMF, $\square$ for LiCL + RBr in acetone, O for LiBr + RBr in acetone; ordinates are experimental $\Delta S^{\ddagger}$ (Table I); lines are least-squares lines. (The DMF data do not define a line.) Abscissas: 2(a) Ingold's calculated $\Delta S^{\ddagger}$ (ref 15); (b) Abraham's calculated $\Delta S^{\ddagger}$ (ref 16); (c) MW of alkyl group, a measure of solvent volume excluded by alkyl group.

tylene. Following these criticisms, Cook and Parker measured the *t*-BuBr reaction in both dimethylformamide with Et_4NCl and acetone with $(n\text{-}Bu)_4NCl$.[25] The $E_{t\text{-}Bu}$ value of 4.01 in Table II is based on the DMF data using the Cook and Parker values for the fraction of substitution. Unfortunately these data fail to clear up the confusion. As can be seen in Table I the $E_{t\text{-}Bu}$ based on runs in DMF, and thus a value that is supposed to give a corrected S_N2 rate also predicts correctly the *total* E2 + S_N2 rates for all the acetone runs; this it should not do. The Cook and Parker data for acetone are not directly comparable with the Hughes et al.[8] data using LiCl, but an indirect comparison can be made. Starting with the Cook and Parker $k_{25} = 2.9 \times 10^{-6}$ (from the Arrhenius equation) and increasing by 20% to allow for incomplete dissociation of quaternary chloride gives a corrected rate of 3.5×10^{-6}. Starting with the Hughes et al. value of 3.1×10^{-7} (Table I) correcting by 875 for the LiCl/free Cl$^-$ ratio[25] and by 0.05 for 5% S_N2[25] gives a corrected value of 14×10^{-6}, in reasonable agreement considering the technical problems. Thus the reported rate constants for *t*-Bu must be corrected downward if they are to represent substitution.

In order to set an upper limit for the rate of the *tert*-butyl halide substitution reactions we have "corrected" each $k(25$ °C) rate constant for *t*-Bu by a factor of $^1/_{15}$ as explained in the footnotes to Table II. This gives an average $E_{t\text{-}Bu} = 5.6$, which should be a reasonably valid estimate of a halogen substitution process whether occurring by S_N2 or by some other mechanism.

Molecular Mechanics Calculations[32-42]

We define the steric energy of a conformation of a molecule in terms of bond, angle, and torsional distortions plus nonbonded repulsions and attractions as calculated from a force field. Steric energies have arbitrary elements which depend on the choice of constants and functions used in the force field. They usually exceed strain energies, but not always.[41] The relationship between steric energies and heats of formation is given by

$$\Delta H_f{}^{\circ} = SE + SM + \Sigma GI \quad (3)$$

The SM term is a small statistical mechanical correction for the presence of a population of conformers of comparable energy,[39,42] and ΣGI is a set of group increment terms for the structural elements present. These are specific for a given force field. Heats of formation of alkanes are reproduced by eq 3 using a group increment summation based on a count of the number of CH_3, CH_2, CH, and C groups present.[6,36-39] A given force field and its specific group increments may be parametrized for any temperature. The force fields we use have been parametrized for the gas phase at 25 °C.

We calculate $\Delta H_i^{\ddagger}$ by the equations

$$\Delta H_i^{\ddagger} = SE_{it} - SE_i + C_{GIN}$$
$$C_{GIN} = \Sigma GI_{it} - \Sigma GI_i \qquad (4)$$

where the subscript *it* refers to the steric energy or the group increments for the transition state of alkyl group *i*. Double differences

$$\Delta H_i^{\ddagger} - \Delta H_{std}^{\ddagger} = \Delta\Delta SE_i$$
$$= (SE_{it} - SE_i) - (SE_{std\ t} - SE_{std}) \qquad (5)$$

permit cancellation of the C_{GIi} constants providing that structural similarity is close. The relationship should be good in comparing primary halides, RCH_2Br, of the β series. The relationship may not be valid for the α series where carbon atoms replace hydrogen atoms at the reaction center.

As a result of this fundamental requirement, the data set is too small to define a force field properly and the experimental data can in principle be matched to any desired level of precision. This is not the whole story, though. The force field constants and functions must also be consistent with other systems. We have explored a fairly wide range of values and find that a useful and consistent picture emerges. These pertain specifically to the reaction $RBr \rightarrow Br-R-Br$. We begin by presenting results given by one reasonable force field (designated *J*) and summarized later in Table III. The calculations are based on complete relaxation, that is, all $3N - 6$ internal coordinates were adjusted for each conformation.

The $\Delta\Delta SE_i$ values are presented in Table II and they do indeed give a satisfactory account of the E_i values for the β series. We note in passing that we have made no calculations of $\Delta S^{\ddagger}$; when correct values become available some force field adjustments may be needed to lower the range of the $\Delta\Delta SE_i$ values. For present purposes the numbers are adequate.

The energies ΔSE_i for a given reaction include estimates of all steric energy changes on going from RBr to $Br-R-Br$ including bond, angle, and torsion deformations. The ΔSE_i do not take into account the energy changes attendant upon forming the bonds (or pseudobonds) $Br\cdots C_\alpha\cdots Br$, and such energies are to be included in the C_{GI} term for the reaction.

We consider now the lack of correspondence between E_i and $\Delta\Delta SE_i$ for the α series. The steric hindrance of ethyl compared to methyl halides as reported in Table II predicts a factor of 35 000 in relative rates. Experimental values are about 60. No reasonable choice of the force field can entirely reconcile the discrepancy; variations we have investigated gave a minimum value of about 7000.

At the other end the reactivity of *t*-BuBr is much higher than the steric factors will allow. Even with a more "liberal" force field that allows a 50% bond extension the steric energy is still 3 kcal too high. Therefore we conclude that the reactivity of the α series is strongly influenced by factors other than steric strain.

We list four, perhaps not entirely independent: hybridization, polar effects, solvation, and bond energies. We dismiss the last two. The difference in bond dissociation energy between CH_3Br and *t*-BuBr is only about 3 kcal.[43] This factor may contribute, but the effect would be difficult to sort out.

Solvation is a differential effect; we dismiss it because we have no good way to estimate it, not because it is necessarily unimportant.

By hybridization we mean the change in ΔH_f° associated with the changes in relative numbers of CH_3, CH_2, CH, and C groups and corrected for steric strains: the difference in ΔH_f° between $(CH_3)_2CHCH_2CH(CH_3)_2$ and $CH_3(CH_2)_7$-CH_3, for example. Our estimates of strain-free group increments are −10.00 (CH_3), −5.15 (CH_2), −2.40 (CH), and −0.54 (C).[41] These are not to be confused with group increments suitable for use in eq 3. Changing a H into a C group involves a greater energy increment for $CH_3 \rightarrow CH_2$ (4.85) than for $CH \rightarrow C$ (1.86). This hybridization factor tends to stabilize CH_3Br in comparison with CH_3CH_2Br; it would make methyl bromide less reactive compared to ethyl.

Polar factors may also be large for the α series. Ingold's group postulated a small retardation by electron-releasing methyl groups in going from methyl to *tert*-butyl, and their rationale seems based entirely on a need to bolster a too feeble steric effect calculated for *tert*-butyl.[15] We would argue conversely that polar factors in the α series should be large and that methyl substitution should accelerate. Schleyer's group has suggested a factor of 10^8 increase in solvolysis rate, or about 11 kcal/mol of stabilization, on going from a secondary to a tertiary carbocation intermediate.[44,45] In order to provide a smooth transition in substitution mechanism the S_N2 reaction should show similar influences though in diminished degree.[46,47]

If the influence extends throughout the series, it would provide a second factor that would make methyl halides less reactive relative to ethyl halides than purely steric hindrance could predict.

Polar effects in the β series are probably small. The ρ value for $C_6H_5CH_2Cl + I^-$ in acetone is +0.81;[48] however, the opposite effect has been reported for alkyl groups, *p*-methyl and *p*-*tert*-butylbenzyl bromide reacting 20–40% faster than benzyl bromide.[49,50] Likewise *t*-BuC≡CCH_2Br reacts about 25% faster with KI in acetone than does *n*-BuC≡CCH_2Br.[51] This corresponds to a $p^* = -0.6$,[52] a polar effect being transmitted across a triple bond while a steric effect is not. Even assuming an improbably large p^* value of −2, the relative polar effect between CH_3CH_2Br and $(CH_3)_3CCH_2Br$ would be log $k_{rel} = 0.3 \times 2$, a maximum factor of 4 acceleration for *tert*-butyl; a factor of 2 would be more probable ($p = -1$). An effect so small would be obscured by the large steric effects.

The Force Field

Attempts have been made to calculate rotational barriers and conformational populations of halogen compounds, and Meyer and Allinger have proposed a comprehensive halogen force field.[53-59] There are not enough structural and thermodynamic data to determine more than approximate values of the parameters.

For alkyl bromides we have started with the Schleyer 1973 alkane force field.[6,39] In spite of known shortcomings, such as a somewhat too stiff $H\cdots H$ nonbonded function,[60] this force field has given good results in other studies. To the alkane force field must be added appropriate values for C–Br stretching, for C–C–Br and H–C–Br bending, and for Br–C–C–X torsional barriers, plus suitable $H\cdots Br$ and $C\cdots Br$ nonbonding interations. The values we used are summarized in Table III.

X-ray crystallographic values of the aliphatic C–Br bond length range from 1.93 to more than 2.0 Å;[61] electron diffraction values are about 1.94–1.95 Å.[56,62] Reported force constants from normal coordinate analyses are 2.79[63] and 2.63 for –CH_2Br and 2.31 for –CHBr.[56] We have adopted Meyer and Allinger's values of 1.94 for the reference and 2.6 mdyn $Å^{-1}$ for the force constant.[59]
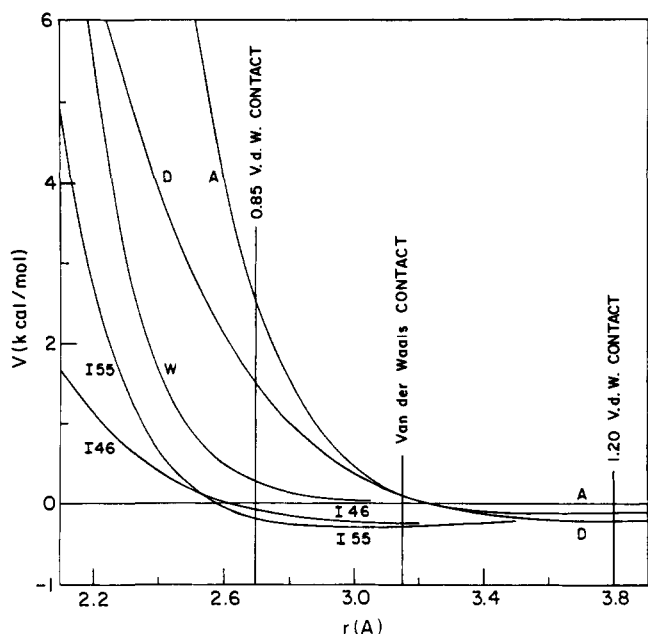
Figure 3. Representative nonbonded functions for H···Br interactions. 146 (ref 1), 155 (ref 15), W (ref 70), D (this work), A (ref 58). The van der Waals radii, 1.95 + 1.20 (ref 71).
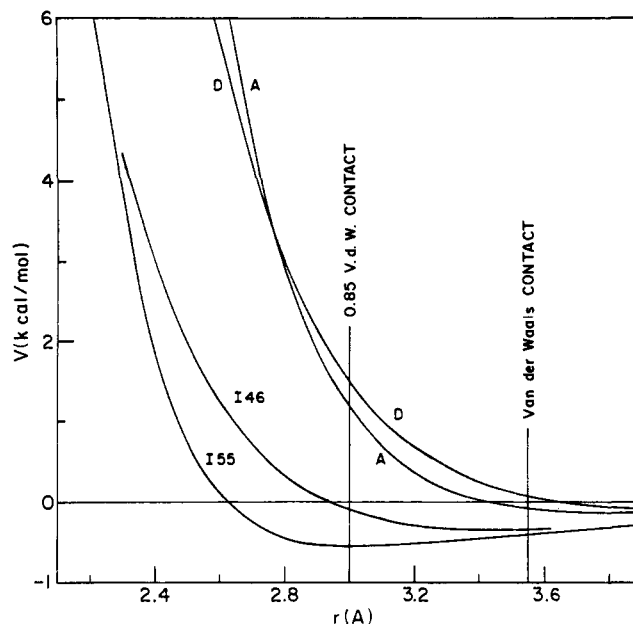

Figure 4. Representative nonbonded function for C···Br interaction; van der Waals contact is 3.55 (1.95 + 0.77 + 0.8). See Figure 3 for references.

Table III. The Force Field[a]

Bond terms	Force field J	
	Ref	Force const
C–Br	1.94 Å	2.6
H–C–Br	110°	1.15×10^{-4}
C–C–Br	110°	1.25×10^{-4}
C_α···$Br^{-1/2}$	1.94 Å	6.6×10^{-2}
H–C_α···$Br^{-1/2}$	105°	6×10^{-5}
C–C_α···$Br^{-1/2}$	105°	6×10^{-5}
$Br^{-1/2}$···C_α···$Br^{-1/2}$	180°	3×10^{-5}
H–C_α–H	109.5°	6.7×10^{-5}
H–C_α–C	109.5°	8.2×10^{-5}
C–C_α–C	109.5°	1.2×10^{-4}

Nonbonded Functions

H···Br	$V = -4.65r^{-6} + 790$ $\exp(-3.77r)$	$V = -10.55r^{-6} + 44.49$ $\exp(-2.62r)$
C···Br	$V = -5.62r^{-6} + 630$ $\exp(-3.53r)$	$V = -7.74r^{-6} + 99.47$ $\exp(-3.53r)$

[a] For all C and H terms we used the Schleyer 1973 force field.[6,39]
[b] Units: bond stretch, mdyn Å⁻¹ molecule⁻¹; angles, mdyn Å deg⁻² molecule⁻¹; nonbonded functions, mdyn Å⁷ molecule⁻¹ and Å; 143.7 mdyn Å molecule⁻¹ = 1 kcal/mol.

Reported bending force constants for C–C–Br are 0.86,[63] 0.91, and 1.05[56] mdyn Å rad⁻² molecule⁻¹, and for H–C–Br are 0.69 and 0.74.[56] The values we have adopted in Table III correspond to 0.41 and 0.38 so that $\partial^2 V/\partial p^2_{bend}$, the effective bending constants, will approach the reported values. We used the H–C–C–C torsion value for X–C–C–Br since the value reported by Meyer and Allinger is little different. Normal coordinate analyses for RCl and for RI were checked for comparisons with those for RBr.[63-69]

Several nonbonded functions have been proposed for H···Br and for C···Br.[1,15,53-58,70] There is no agreed-upon procedure for defining nonbonded functions suitable for molecular mechanics. Until experimental data become available to permit refinements, we must construct the functions by analogy. Meyer and Allinger prefer to base analogy on the Hill function.[58] We have chosen to base analogy more directly on

functions that have proven useful for H···H and C···H interactions. These tend to have attractive forces of −0.1 to −0.2 kcal/mol⁻¹ at a minimum $r_1 \simeq 120\%$ of r_c, the van der Waals crystal contact distance, and with dV/dr a minimum at r_1. For H···Br, $r_1 = 3.80$ Å, and for C···Br, $r_1 = 4.20$ Å. The repulsive energy at $0.85r_c$ is of the order of 1 or 2 kcal/mol. The constants we have chosen for the H···Br and the C···Br nonbonded interactions make $V = 1.5$ kcal/mol at r_2, taken as 2.7 Å for H···Br and as 3.0 Å for C···Br. Our functions and other representative functions are shown in Figures 3 and 4. The Meyer and Allinger functions are similar while the Westheimer H···Br function is considerably weaker. We believe that the Westheimer function is too weak, and the Ingold functions are unrealistic.

The r's we chose for the minimum somewhat exceed the sum of the "true" van der Waals radii recommended by Allinger (3.60 Å for H···Br and 3.85 Å for C···Br).[36] Since the minimum is long and shallow, the effect of choice of r_1 on curve shape may be more significant than is the location of the precise minimum. For example, changing the control parameters r_1 to 3.6 Å and leaving V (min) = −0.2 and $r_2 = 2.7$ Å with $V = +1.5$ yields a somewhat softer curve for $r > 2.7$ Å: $V = 0.23$ instead of 0.39 at $r = 3.0$ Å, which is in the critical repulsive range.

Our force field gives SE = 7.40 kcal/mol for the eclipsed conformer of neopentyl bromide (fully relaxed) and a barrier of 4.00 kcal/mol; observed 6.0;[72] for 2,3,3-trimethyl-2-tri-methyl-2-bromobutane we get a 16.90 − 9.90 = 7.00 barrier, while observed is 10.8.[72] We would prefer closer agreement and could get it by stiffening the bending of the C–C–Br bond. We decided not to do so since the effect on relative ground state SE's is small, since our effective force constant is already as stiff as is reported in normal coordinate analyses, and since a detailed adjustment of the force field is a major undertaking not warranted by present requirements.

Choices of suitable force constants for the transition states were based upon the following considerations. We first made calculations using fixed geometry at the reaction center but using a series of C_α···Br distances and a series of Br···C_α···Br angles. The alkyl groups were allowed full relaxation. The calculations showed that bond bending of Br···C_α···Br was the most effective way to relieve strain in the β series. Bond

Table IV. Steric Energies of Alkyl Bromides and of Transition States

	RBr	Br–R–Br
Me	0	7.41
Et	1.08	14.69
n-Pr	1.66	15.31
i-Bu	2.61	18.09
neo-Pe	3.40	24.04
i-Pr	1.90	19.67
t-Bu	2.53	27.91

stretching of $C_\alpha \cdots Br$ was obviously necessary for *tert*-butyl. Since a fixed geometry is clearly a poor model we turned our attention to assigning plausible values to the rest of the terms needed to allow complete relaxation at the reaction center.

Some of these constants can assume any desired arbitrary value since they add a nearly constant energy for all alkyl groups. The $C_\beta-C_\alpha-C_\beta$, $C_\beta-C_\alpha-H_\alpha$, $H_\alpha-C_\alpha-H_\alpha$ force constants form such a group. These were set at $\frac{2}{3}$ of their normal value since bonding force constants at sp^2 carbon atoms are smaller than at sp^3. Other terms affect the range of steric energies within the β series. These include the constants for $C_\beta-C_\alpha\cdots Br$, $H_\alpha-C_\alpha\cdots Br$, and $Br\cdots C_\alpha\cdots Br$. The ratios of these constants also affect the k_{Me}/k_{Et} ratio. We softened them a bit by using initially a 100° reference angle instead of a tetrahedral reference, but we subsequently raised the reference to 105° to reduce the methyl/ethyl gap. Suitable force constants are about half the constant for C–C–C bending except that $Br\cdots C_\alpha\cdots Br$ required a weaker constant. These various constants cannot be changed by a factor much more than 2 without causing serious distortion. The value chosen for $Br\cdots C_\alpha\cdots Br$ has a major effect on the relative $\Delta\Delta SE_i$ values for the β series.

The nonbonded functions used for $H\cdots Br^{-1/2}$ and $C\cdots Br^{-1/2}$ were the same as used for RBr simply because we have no basis for making a better choice. The semiionic halogen will be larger and presumably softer. There will be Coulombic effects, attractive between $H\cdots Br$ and repulsive between $C\cdots Br$. The critical steric region around the reactive center is not very large

and the relative constancy of the Coulombic terms together with some tendency for cancellation mitigates the effect of omitting these.

The remaining problem was to go as far as possible in accommodating *i*-Pr and *t*-Bu in the same force field as the β series. We had used separate ad hoc references distances for $C_\alpha\cdots Br$, one for ethyl and the β series, others for *i*-Pr and *t*-Bu. As an alternative we tried the effect of setting the force constant for stretching the $C_\alpha\cdots Br$ bond to a very low value, 0.1 mdyn Å^{-1}, about $\frac{1}{25}$ the normal C–Br force constant. Whether this value is realistic we cannot demonstrate quantitatively, but the steric account given by the force field is plausible. Published values of the energy of the $(F-CH_3-F)^{-1}$ system as a function of C–F distance are inconsistent. The CNDO values indicate a force constant $k = 3.4$ mdyn Å^{-1} $(0.5k(1.6 - 1.344)^2 - 0.5(1.439 - 1.344)^2 = (64.7244 - 64.7025) \times 627/143.7)$.[18] Ab initio calculations for the same system give a negative value for k.[20] Ab initio calculation for $(H-CH-F)^-$ gives $k = 1.0$.[18] From scaled values of the diagram for the $H^- + H_2CO$ reaction we find $k \sim 0.7$.[72] Qualitatively it is reasonable to suppose that the bonding in $(Br-R-Br)^-$ is weak and the force constant also weak.

Steric Factors in S$_N$2 Reactions

Steric energies of starting alkyl bromides and of transition states are reported in Table IV. The resultant $\Delta\Delta SE$ values are listed in Table II. Figures 5 and 6 and Table V describe the major features of the geometries of the transition states of S$_N$2 reactions as defined by the force field in Table III. The origins of the steric energies are summarized in Table VI.

The general features of the geometry can be predicted qualitatively. Steric repulsions between the bromine atoms and the alkyl group govern and are removed principally by bending. The status of the *tert*-butyl group is consistent with its inertness and ambiguity toward S$_N$2 reactions. Steric effects are so large that the $C_\alpha\cdots Br$ bonds must become greatly elongated, effectively requiring partial ionization.

We note that our model for the transition state applies the force field symmetrically with respect to the bromine atoms.

Table V. Transition State Geometries Br–R–Br

General	Figure 5	*n*-Pr	neo-Pe	*i*-Bu	*i*-Pr	*t*-Bu
			Bonded			
C_α–Br	C_3–Br$_{23,24}$	2.22	2.28	2.23	2.40	2.69
Br–C_α–Br	Br$_{23}$–C_3–Br$_{24}$	161.4	143.2	155.3	158.3	180.0
H_α–C_α–H_α	H_4–C_3–H_5	123.1	126.6	123.6		
H_α–C_α–C_β	$H_{4,5}$–C_3–C_6	118.5	116.6	117.9	122.2	
C_β–C_α–C_β					115.6	120.0
H_α–C_α–Br	H_4–C_3–Br$_{23}$	86.6	79.7	86.5	79.4	
	H_5–C_3–Br$_{23}$	84.7	79.7	86.5		
	H_4–C_3–Br$_{24}$	86.6	84.3	81.7	78.9	
	H_5–C_3–Br$_{24}$	84.7	84.3	81.7		
C_β–C_α–Br	C_6–C_3–Br$_{23}$	99.2	110.5	105.9	95.6	90.0
	C_6–C_3–Br$_{24}$	99.2	106.3	99.0	95.9	
C_α–C_β–C_γ	C_3–C_6–C_8	113.2	110.5	113.0		
	C_3–C_6–C_{13}		110.5	113.0		
	C_3–C_6–C_{18}		114.1			
			Nonbonded			
$C_\gamma\cdots$Br	$C_8\cdots$Br$_{24}$		3.38	3.38		
$H_\gamma\cdots$Br	$H_{11}\cdots$Br$_{24}$		2.84	2.93		
$C_\gamma\cdots$Br	$C_{18}\cdots$Br$_{24}$		3.35	3.40		
$H_\gamma\cdots$Br	$H_{15}\cdots$Br$_{24}$		2.80	2.91		
$C_\gamma\cdots$Br	$C_{18}\cdots$Br$_{23}$	(eclipsed)	3.07			
$H_\gamma\cdots$Br	$H_{20}\cdots$Br$_{23}$		2.86			
$H_\gamma\cdots$Br	$H_{21}\cdots$Br$_{23}$		2.83			
$H_\alpha\cdots$Br	(eclipsed)			2.56		
$H_\beta\cdots$Br		2.72 (2)[a]			2.80 (4)[a]	2.73 (6)[a]
$C_\beta\cdots$Br		3.60 (2)[a]				

[a] Number of interactions if more than 1.

Table VI. Steric Energies of Transition States

	n-Pr	i-Bu	neo-Pe	i-Pr	t-Bu
C–C str	0.21	0.40	0.80	0.17	0.24
H–C–C bend	0.14	0.51	0.28	0.26	0.50
H–C–H bend	0.26	0.11	0.31	0.30	0.57
C–C–C bend	0.09	0.21	0.58		
Torsion	1.30	1.18	1.15	2.14	4.18
C_α–Br str	1.16	1.28	1.66	3.06	8.13
H–C_α–Br	6.49	7.54	9.33	5.75	
C–C_α–Br	0.29	0.16	0.14	1.48	5.82
Br–C_α–Br	0.74	1.31	2.92	1.01	
H–C_α–H	0.89	0.96	1.41		
H–C_α–C	0.95	0.83	0.60	1.90	
C–C_α–C				0.32	2.85
Total bonded	12.52	14.49	19.18	16.39	22.29
H⋯H	-0.23^a	−0.49	−0.96	−0.33	−0.48
	0.98^a	1.65	1.67	0.40	0.10
H⋯C	−0.06	−0.17	−0.37	−0.06	−0.30
	0.13	0.37	1.30	0.05	0.25
H⋯Br	−1.01	−1.72	−1.84	−0.86	−1.97
	2.84	3.59	3.57	4.07	8.06
C⋯Br	0.09	−0.18	−0.28		
		0.56	1.78		
Total nonbonded	2.74	3.61	4.87	3.27	5.66

^{a} The two values given throughout are respectively the separate sums of the attractive and of the repulsive nonbonded interactions.
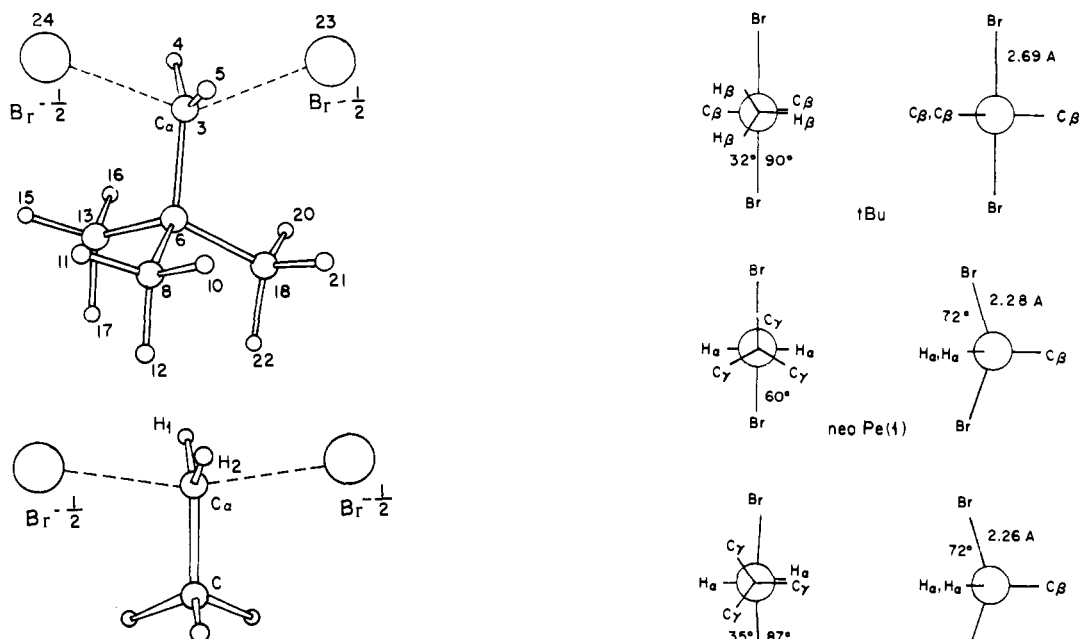

Figure 5. Neopentyl bromide and ethyl bromide transition states, force field J.

In particular we take into account all ten angles at the trigonal bipyramidal carbon, C_α. This tends to make the equatorial plane a plane of symmetry, although some departures do occur depending on the particular force field and on the alkyl halide.

Is the quasi-symmetrical structure an energy maximum? We have sought an answer on steric grounds by reducing the symmetry imposed on our model of the transition states. We set to zero the force constants k_i for all equatorial-axial angles, the C_β–C_α–$Br^{-1/2}$ and/or H_α–C_α–$Br^{-1/2}$ angles for the bromines, and replaced them by Buckingham potentials with −0.1 kcal/mol attraction at the normal angle and with the same 90° repulsion as given by the J force field. In contrast to the J force field, which imposes symmetry through the now omitted bending angles, the modified force field makes the angular forces on the two bromines equivalent without forcing symmetry.
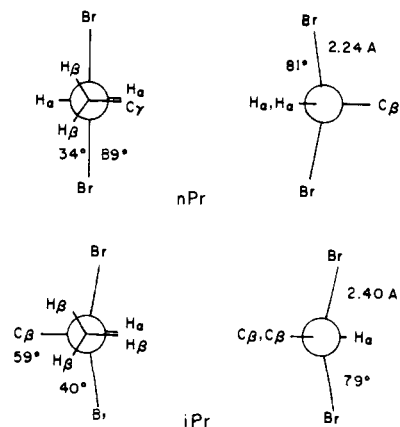

Figure 6. Torsions and angles for representative transition states, force field J.

While overall consequences of the modified force field differ from those of the *J* force field, the calculations show that models with unequal $C_\alpha-Br^{-1/2}$ bond distances are lower in energy by several kcal/mol. For each alkyl group the symmetrical or quasi-symmetrical structures, Figures 5 and 6, represent energy maxima. Unless the several force fields we have examined are in serious error, this conclusion is true for the several S_N2 reactions considered here. Perhaps we should also emphasize that our calculations do not establish whether or not there are stable complexes elsewhere along the reaction paths.

The details of the energy distribution (Table VI) are less easy to predict than changes in geometries. With the neopentyl group the various force fields we have tested agree in assigning almost equal energies to the "eclipsed" and "staggered" conformers (1) and (2) in Figure 6. With the apparently analogous isobutyl group the "H eclipsed" form is clearly of lower energy. The staggered conformer can be studied by "freezing" the rotation about the $C_\alpha-C_\beta$ bond, but when released, the conformation reverts to eclipsed.

The results obtained with fully relaxed models are in marked contrast to those obtained with rigid models. In their Table III[1] Ingold's group lists many H···Br nonbonded distances for the transition states shorter than 2.5 Å and some as short as 2.15 Å. These are based on an assumed $C_\alpha···Br^{-1/2}$ distance of 2.32 Å. In further calculations the t-Bu···$Br^{-1/2}$ distance was increased to 2.39 Å, a value we would consider much too small, yet their calculated steric energy was only 2.2 kcal/mol.

In the more refined calculations described in the 1955 paper[15] angle bending was included; the $Br-C_\alpha-Br$ angle calculated for neo-Pe was 165°. The $C_\alpha-Br^{-1/2}$ distance was in the 2.25–2.30 Å range. The steric energy calculated for neo-Pe was 14 kcal, much too large, while that for t-bu was only 2.8 kcal, much too small.

With relaxed models the H···Br nonbonded distances are longer than 2.8 Å, that is, longer than 90% of the crystal van der Waals contact distances, the exceptions being the short distance 2.56 Å for the eclipsed H···Br atom pair in Br-i-Bu-Br and the relatively short 2.75 Å distance in Br···n-Pr···Br. To confound easy qualitative predictions the shortest distances do not necessarily occur with the most hindered alkyl groups. Tables V and VI present a number of other interesting features which there is not space to discuss.

Changes in the force field produce changes in steric energies and changes in geometry. Except for force fields which lead to gross distortions, those we have examined change the angles only a few degrees, and progressions shown in Table VI tend to remain in step. Perhaps the success of molecular mechanics in treating steric factors is predicated on the same factors that Dunitz and Bürgi[53,73–75] have been developing by comparison of crystal structures. Atoms in molecules are of limited compressibility and have directed valences; hence any systematic way of treating this fact will give useful insights into molecular behavior.

Computer Programs

The work utilized computer programs developed in this laboratory, specifically ACTENG,[76] GENLSS,[76] and MOL-MEC[39,78,79] and associated programs.

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 31. Rate Constants for Spin Trapping. 1. Primary Alkyl Radicals[1]

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Abstract: Rate constants for the addition of primary alkyl radicals to most of the commonly employed spin traps have been determined at 40 °C using the [1-^{13}C]-5-hexenyl radical as the primary standard. In the presence of a spin trap there is a competition between direct addition of this radical to give a ^{13}C labeled spin adduct and its cyclization to the cyclopentylmethyl radical which, when it adds to the trap, gives an unlabeled spin adduct. The results obtained with this radical have been extended by means of competitive experiments using pairs of spin traps and the 1-hexyl radical. Additional rate data has been obtained by measurement of spin adduct concentrations under steady-state conditions.

In the EPR spectroscopic technique of "spin trapping", a transient radical, R·, is "visualized" by allowing it to add to a spin trap, T, and so form a persistent spin adduct, RT·.[3]

$$R + T \cdot \rightarrow RT \cdot \qquad (1)$$

This technique has been used qualitatively to detect and identify reactive free radicals for several years.[3] However, the fact that a spin adduct is observed when a trap is added to some particular reaction system is not of as much help in deducing the reaction mechanism as might be supposed. This is partly because EPR spectroscopy is such an extremely sensitive probe for radicals that a spin trapping experiment may yield a "positive" result on a minor side reaction, while the main reaction is overlooked if it is nonradical, or even when it does involve radicals if they are not readily trapped or yield nonpersistent spin adducts. The ambiguity of a positive result can be largely avoided if kinetic data are available regarding the rates of spin trapping of the radicals in question *and* the rates at which the spin adducts so formed are themselves destroyed. There are relatively few rate data available for spin trapping,[4-11] and there is even less information available concerning the rates at which spin adducts are destroyed. In view of the great potential of spin trapping, we have begun a program to determine accurate rate constants for the trapping of some of the more commonly encountered radicals. This, the first paper,[1] is devoted to the trapping of primary alkyl radicals in benzene.

The 5-hexenyl radical, H·, provides the mainstay for the present work. This radical isomerizes irreversibly to yield the cyclopentylmethyl radical, C·.[12] The rate constant for this cyclization, k_c, was initially estimated at ambient temperatures by combining some product studies of Walling et al.[13] with a rotating-sector kinetic study of our own on the trialkyltin hydride–alkyl halide reaction.[14] We subsequently investigated this cyclization by kinetic EPR spectroscopy and obtained Arrhenius parameters which confirmed the earlier results.[15]

Since both H· and C· are primary alkyls, the spin adducts that they form with any particular spin trap will have similar properties, i.e., similar kinetic and thermodynamic stabilities, which is an advantage, and similar EPR spectra, which is a handicap. However, a nice distinction between the spectra of the two spin adducts, HT· and CT·, can be obtained by labeling the 5-hexenyl radical with carbon-13 ($I = \frac{1}{2}$) in the 1 position. In most cases, hyperfine splitting (hfs) by this ^{13}C atom should be detectable in the EPR spectrum of HT· because of the proximity of the ^{13}C to the orbital containing the unpaired electron in this adduct. However, in CT· the ^{13}C will be too remote from the unpaired electron to produce any appreciably hyperfine splitting. The reaction system depicted in Scheme I allows the rate constant for the spin trapping of H· to be

Scheme I
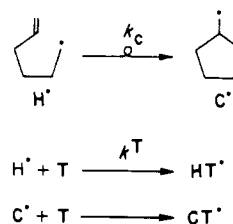
calculated from the trap concentration and the measured ratio of the initial rates of formation of the two spin adducts, i.e.,

$$k^T = \frac{k_c}{[T]} \frac{(d[HT \cdot]/dt)_{t \to 0}}{(d[CT \cdot]/dt)_{t \to 0}} \qquad (Ia)$$

Implicit in this equation is the assumption that *all* of the alkyl radicals formed are captured by the spin trap (vide infra). As long as the total concentration of the adducts does not approach the steady-state level, this equation is equivalent to

$$k^T = \frac{k_c[HT \cdot]}{[T][CT \cdot]} \qquad (Ib)$$