

Mechanism of Substitution at a Saturated Carbon Atom. Part XLIX.
Analysis of Steric and Polar Effects of Alkyl Groups in Bimolecular
Nucleophilic Substitution, with Special Reference to Halogen Exchanges.*

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In continuation of the work (1946) of Dostrovsky, Hughes, and Ingold on the subject indicated in the title, the assumptions underlying their analysis are critically examined. One major modification of method is then introduced. On this basis, their calculations of the energetic effects produced by alkyl groups on the kinetics of the bromine-exchange reaction are revised. And they are extended to substitutions involving chlorine and iodine. They are also extended by a calculation of the associated entropic effects. The results are as follows.

In these reactions, the steric energetic effects of the alkyl groups are always retarding. But, contrary to earlier ideas of steric hindrance, such effects depend only slightly, and not always in the preconceived sense, on the sizes of the halogen atoms. They depend strongly on the structures of the alkyl groups, in which successive β -substitution starts by being less important, but, again contrary to older preconceptions, ends by being much more important, than successive α -substitution. The polar energetic effects of the alkyl groups are retarding, and are associated almost exclusively with α -substitution.

Three kinds of structural entropic effects, called ponderal,[†] steric, and polar, are recognised, which depend on the incidence and distribution of mass, bulk, and charge, respectively. The ponderal effect, which would be exerted by massive, but non-space-filling, non-polar particles, such as neutrons added by isotopic substitution, is retarding in general, though a sufficient accumulation of new masses, near the reaction centre will weaken this effect, and could conceivably reverse it. Contrary, again, to elementary preconceptions, the steric entropic effect is accelerating if the steric thrust on the attacking reagent is directly outwards, but retarding if the main effect of it is to deflect the reagent sideways. The polar entropic effects of alkyl groups are negligible.

The quantitative analysis is made from first principles, without the use of adjustable constants, excepting one polar constant for the whole family of groups and reactions. The energies of activation and frequency factors thus calculated are compared with the available experimental values. The agreement is good generally, though only fair for reactions of the *neopentyl* group; and a plausible reason for the lower accuracy obtained with this last group is suggested. Calculated effects of alkyl structure on the rates themselves agree with observed rates to a factor of 2.5 over that range, 10^4 , of rates which excludes the *neopentyl* group, and to a factor of 5.5 over the complete range, 10^7 , of rates which includes this group. There is thus some experimental support for the genuineness of the pattern of effects described by theory. Proposed extensions of the theoretical treatment, *e.g.*, to bimolecular nucleophilic substitutions of a more general character are briefly indicated.

FOR some decades the theory of steric hindrance remained undeveloped, because its dependence on the details of reaction mechanism was not understood, and in any case such details were unknown. Later, when the mechanisms of some general reactions became known well enough to permit a geometrical and electronic description of their transition states, it became possible, not only to foretell from the mechanism in operation whether steric hindrance would, or would not, be present in principle (Hughes, *Trans. Faraday Soc.*,

* Part XLVIII, preceding paper. † Cf. footnote, p. 3216.

1941, **37**, 620; Day and Ingold, *ibid.*, p. 686), but also to make a beginning on the problem of quantitatively calculating expected steric effects on reaction rate.

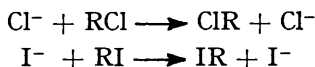
Such calculations have been reported for bimolecular nucleophilic substitutions in a series of simple alkyl halides (Hughes, *loc. cit.*; Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173), but at a time when the experimental material available for comparison with the calculated results was comparatively slight. However, the calculations have since been extended; and additional experimental results have now become available, as recorded in the accompanying papers. In this paper we report the further calculations, and with their aid discuss the new experimental material.

The previous calculations were developed in detail in the example of the bromine-exchange reaction,



for the seven alkyl groups, which compose the α - and the β -methylated series of branching homologues, Me, Et, Pr¹, Bu¹, and Et, Pr², Bu¹, *neo*Pe (*neopentyl*). The object was to compute the energy of mutual compression of all atoms not directly bonded together, both in the transition state of substitution, and in the initial alkyl bromide molecule, and thus to obtain the excess of non-bonding energy involved in the formation of the transition state. This excess represented the calculated contribution of steric hindrance to the activation energy of the reaction. The simplifications employed precluded any attempt to discuss, even qualitatively, the effect of steric hindrance on the entropy of activation.

In the present extension of this work, our first proceeding will be to set out the assumptions and approximations involved in the previous calculations, and to reconsider some of the more questionable of them, particularly as to the possible influence of any such uncertainties on the results. We shall then introduce one major modification of method, and on this basis revise the former calculations. We shall also extend them, in their revised form, to the two other exchange reactions,



in order to have a range of theoretical results more nearly representative of the experimental data now available. And we shall further extend them to include a quantitative discussion, the first of its kind, so far as our knowledge of the literature extends, of structural effects, including those of steric hindrance, on entropy of activation, and so on the frequency factor of reaction rate. Finally, we shall summarize the observations, and discuss them in the light of the calculations.

(A) CONSIDERATION OF ASSUMPTIONS AND APPROXIMATIONS.

(a) *Statement of Initial Assumptions and Approximations.*—The first set of geometrical assumptions employed by Dostrovsky, Hughes, and Ingold (*loc. cit.*) was as follows. The initial molecules were taken to have normal covalent bond-lengths, and tetrahedral bond-angles. In the transition states, the same assumption was made for all bonds except those of the α -carbon atom, whose three bonds to hydrogen or carbon were given a normal length, but were taken as trigonally disposed in a plane, to which the oppositely directed, semi-ionic semi-bonds to the two halogen atoms were perpendicular. The common length of the equivalent semi-bonds had to be specially computed, as noted below. The geometry so far specified was assumed to be determined entirely by the bonding forces. Non-bonding forces were allowed to determine rotational conformations, but not to stretch or bend bonds. The forms of the resulting transition-states of substitution of the seven alkyl groups considered are diagrammatically represented in the paper cited. It will be convenient to describe this type of model as "stiff," even though rotations are allowed, the reference being to the assumed restrictions on the stretching and bending of bonds by non-bonding forces.

For the computation, from these models, of the various non-bonding pressures, certain dynamical assumptions were necessary. Of the two types of force-law that have been

successfully employed in work on pressure-volume relations, the one involving an exponential, and the other a power-law, repulsive potential, the former was adopted. Specifically, the energy W of non-bonding interaction of any pair of atoms at a nuclear separation r was assumed to be

$$W = -Ar^4 - Br^6 + be^{-r/0.345}$$

the first term representing electrostatic attraction, the second electrokinetic attraction, and the third steric repulsion. The coefficients A and B can be computed from known atomic constants, whilst b has to be evaluated empirically, using the condition that dW/dr vanishes when r equals the van der Waals distance. The length-constant, 0.345 Å, is also empirical, and was found by Born and Mayer to be the best general value for application to a considerable number of kinds of atom-pairs. It was selected in preference to any of the values which have been theoretically derived for certain cases by relatively crude methods of quantum-mechanical approximation.

Van der Waals radii are thus an important part of the empirical basis of the force law. Such radii are well established for large angles χ to the bonding direction, but there is some duality as to their values at small angles. From the almost normal geometry of the molecules of simple derivatives of methane, Pauling deduced such a shortening of the radii at low angles as would remove non-bonding pressure at 35°. Dostrovsky, Hughes, and Ingold, accepting this conclusion, shortened their radii for angles below 90° by $0.4(1 + \cos 2\chi)$ Å, thereby allowing the atoms a van der Waals surface which contracts towards the bonding direction, smoothly taking in Pauling's radius at 35°, and the covalent radius at 0°. For a semi-ionic halogen, the coefficient in the above formula was reduced from 0.4 to 0.2, because it would obviously be reduced to 0.0 in the free halide ion.

Whether or not this assumption of radii contracted at low angles is realistic, it had two convenient effects on the course of the calculations (its effect on their results is discussed below). For, first, it reduced to negligibly small values the non-bonding energies calculated for initial states, thereby enabling energies of steric hindrance to be related to compression energies calculated for transition states only. Secondly, it reduced to negligibility the calculated compression energy of one transition state, *viz.*, that of the substitution involving the methyl radical; and since any experimental assessment of energies of steric hindrance can only be relative, with the case of methyl as an adopted zero, it is convenient to have this energy for the methyl group calculated as zero. The overall simplifying effect was that energy of steric hindrance, though in principle to be calculated as a second difference of the compression energies of four states, could in practice be identified with the compression energy of the relevant transition state only.

Dostrovsky, Hughes, and Ingold estimated the lengths r_t of the semi-bonds to bromine in their transition states by two methods. The first had only intuitive justification, and gave 2.31 Å: compression energies were for the most part calculated with this value. Subsequently, the length was recalculated on the more rational group of assumptions that the energy of activation consists of the energy needed (1) to bring the three preserved C_α -bonds into a plane, (2) to remove solvating solvent displaced by the attack of the bromide ion, (3) to press the latter against the carbon atom to a nuclear separation r_α , (4) to stretch the CBr-bond to an equal length r_α , and (5) to divide the ionic charge equally between the bromine atoms, this last term being negative. It was assumed that energies (1) and (2) vary negligibly with r_α in the relevant range, that energy (5) passes through a stationary value (maximum resonance) at the transition-state distance, that (3) can be calculated as already outlined, and that (4) is given by the Morse function. The total energy was found to be minimal when r_α was 2.25 Å, this being the revised value of the semi-bond length r_t . The calculations were not systematically repeated with this not much altered value, but they were extended in a way which employed it, and, in the extension, the involvement of two slightly different values led to certain minor inconsistencies.

(b) *Effect of Steric Pressure on the Geometry of Transition States.*—Undoubtedly the most dangerous of the above assumptions is that summarised in the term "stiff" as applied to this model, particularly with respect to transition states, in which the important non-bonding pressures are developed. It cannot be true that bonding forces alone determine

the bond lengths and angles, and that then non-bonding forces build up steric energy within the model so determined. They must deform the model, raising the bonding energy and lowering the non-bonding, but in such a way that the total energy is minimised. The effect of the deformation will be to reduce the steric energy, now considered as the excess of total energy, bonding plus non-bonding, above what it would have been in the absence of the non-bonding forces.

To calculate minimised total energy in a transition state, with allowance for the possible bending and stretching of every bond that might be so affected, would be an arduous task. But most of the relief by deformation from non-bonding strain must come from the bending and stretching of the weak semi-bonds, and an energy calculation which allows for this is not unduly tedious. For convenience, we may call the transition-state model in which all degrees of freedom of deformation are permitted in the reaction system, the "plastic" model, even though it allows only the leading elements of the total plasticity of the natural transition state.

In the extension of their calculations mentioned above, Dostrovsky, Hughes, and Ingold contributed a little to the problem of calculating with the "plastic" model. When, as in general, the semi-bonds are both bent and stretched by non-bonding pressures, the bending will usually have a considerably more important energetic effect than the stretching. However, they then saw no easy way to compute the effect of bending. But in the substitutions of the trigonal molecules, methyl bromide and *tert.*-butyl bromide, there is no bending of the semi-bonds of the transition states, and their stretching could be, and was, taken into account by simply adding one more term, the non-bonding energy expressed as a function of r_{α} , to the five previously assumed to compose the activation energy. For methyl bromide there was no non-bonding energy in the transition state, and therefore no stretching of the semi-bonds, and no change of total energy. For *tert.*-butyl bromide, non-bonding compressions stretched the semi-bonds of the transition state by 0.04 Å, and reduced the total energy, and therefore the steric energy, by 0.3 kcal. mole⁻¹.*

The most notable case in which the calculated steric energy was obviously too high was that of *neopentyl* bromide, the discrepancy amounting to about 7 kcal. mole⁻¹, of which about 1 kcal. mole⁻¹ was ascribed to a polar effect. Although bending must occur here, the effect was calculated of allowing the semi-bonds to stretch, but not to bend; and it was found that this reduced the calculated total energy by 1 kcal. mole⁻¹. It was then suggested that an allowance for bending, if one were made, might absorb the major part of the remaining discrepancy of 5 kcal. mole⁻¹, the intuitive reasoning being that, as bending frequencies in molecules are often about one-half of the corresponding stretching frequencies, one might expect the energetic effect of bending to be roughly four times that of stretching, *i.e.*, about 4 kcal. mole⁻¹ in this case.

This seems to have been not a bad guess, to judge from the results, reported in Section C, of our more recent calculations of the bonding and non-bonding energies of transition states as functions of all the degrees of freedom allowed in the "plastic" model. But, before coming to this, two other features of the earlier calculations require reconsideration.

(c) *Forms of the Non-bonding Force Law.*—Dostrovsky, Hughes, and Ingold chose an exponential form of steric interaction energy, $be^{-r/a}$, because theory indicates that the true expression should contain an exponential factor, and because an exponential function, with empirically determined parameters, is a notoriously powerful absorbent of errors arising from neglected power terms and factors; and certainly higher-power terms of electrostatic and electrokinetic types, as well as power factors of steric type, are neglected in their expression for the non-bonding energy. Born and Mayer had shown that the exponential potential combined as necessary with just the leading electrostatic and electrokinetic terms, gives a good account of energy-volume relations in simple ionic crystals (*Z. Physik*, 1932, **75**, 1), and Buckingham that it does the same for those of non-ionic gases and crystals (*Proc. Roy. Soc.*, 1938, *A*, **168**, 264), as has been extensively confirmed by this

* The different figures previously tabulated involve an inconsistency arising from the two estimates of the undeformed semi-bond lengths. But Fig. 6 of the previous paper shows fairly well the basis of the figures here cited.

author and by others subsequently. In the meantime, Westheimer has used the exponential form in successful calculations on a rate process, albeit a physical one, inasmuch as no bonds are formed or broken, *viz.*, the racemisation of 2 : 2'-dihalogenodiphenyl compounds (*J. Chem. Phys.*, 1947, 15, 253; Reiger and Westheimer, *J. Amer. Chem. Soc.*, 1950, 72, 14).

However, it is well known that a power-law repulsive potential, of the form $b'r^{-n}$, with $8 \ll n \ll 14$, is about equally successful in the description of gaseous energy-volume relations; according to Buckingham (*loc. cit.*), any value of n within the limits indicated, if combined with a suitable value of b' , will serve for this purpose. A. G. Evans took n as 9, when he calculated non-bonding energies with the expression $W = -Ar^{-4} + b'r^{-9}$, where the first term is electrostatic, and b' is evaluated from the condition that $dW/dr = 0$ at the van der Waals distance (*Mem. Proc. Manchester Lit. Phil. Soc.*, 1947, 87); though had the omitted electrokinetic term been included, the value of b' would have been considerably altered.

In order to exemplify the effect of changing over to a power-type force-law, we have repeated Dostrovsky, Hughes, and Ingold's calculations for the bromide-ion substitution of methyl and *tert.*-butyl bromides, using, as they did in these especially simple cases, the "plastic" model, but assuming Evans's form of non-bonding potential, with the exception that we have included the leading electrokinetic term, and have redetermined b' accordingly. In these particular illustrative calculations, Dostrovsky, Hughes, and Ingold's assumptions concerning van der Waals radii have not been changed.

For the reaction of methyl bromide, the energy of the transition state, expressed as a function of r_α , is

$$W = C - 158r_\alpha^{-4} - 810r_\alpha^{-6} + 63,740r_\alpha^{-9} + 70.6[e^{-3.28(r_\alpha-1.91)} - 2e^{-1.64(r_\alpha-1.91)}]$$

in kcal./mole, when r_α is in Å. The constant C can be allowed to determine any convenient energy zero. This energy is minimal when $r = 2.45$ Å. Thus the new semi-bond length r_i is 0.2 Å greater than before. There is no significant non-bonding energy in either the initial or the transition state, and hence no energy of steric hindrance.

For the reaction of *tert.*-butyl bromide, there is still no significant non-bonding energy in the initial state. However, the energy of the transition state is raised by non-bonding pressures, one effect of which is to lengthen the semi-bonds. The additional energy, which must now be calculated with the power-type potential, includes, in the first place, six C_β -Br compression terms, each equal to

$$C_C - 39.5r_C^{-4} - 708r_C^{-6} + 17820r_C^{-9}$$

where r_C is the common C_β -Br distance, a geometrically determinate function of r_α , and C_C is a constant, whose inclusion sets the energy zero of these terms at the point at which r_C is the appropriate van der Waals distance, 3.04 Å. The rest of the non-bonding energy consists of six H_β -Br compression terms, each equal to

$$C_H - 17.8r_H^{-4} - 346r_H^{-6} + 7964r_H^{-9}$$

where r_H is the shortest H_β -Br distance, also a calculable function of r_α , and C_H similarly sets the zero of these terms where r_H is the van der Waals distance, here 2.98 Å. The reason why these energy zeros should be taken at the van der Waals distances is explained in the former paper. No larger H_β -Br distances lead to significant contributions to the energy. When these two sets of six terms are re-expressed as functions of r_α , and then added to the previous expression for W , a new function \bar{W} is derived, which has its minimum at $r = 2.53$ Å. The semi-bonds have thus been lengthened, by 0.08 Å, by the steric pressure. The new minimum lies 2.8 kcal. mole⁻¹ above the old minimum. And since the old minimum included no non-bonding energy, and the initial states are calculated to have none, 2.8 kcal./mole represents the energy of steric hindrance of the reaction of *tert.*-butyl bromide.

From their exponential-type potential function, Dostrovsky, Hughes, and Ingold calculated 2.5 kcal. mole⁻¹ as the energy of steric hindrance of this reaction.* The unimportant difference between these two estimates exemplifies the general point that the results

of such calculations are strongly buffered against even considerable variations in the assumed potential function, provided that this is one of those known to give a good description of physical properties, and provided that it is made as dependent as possible on empirical parameters. What has happened in the present illustration is that the stronger repulsive forces assumed in the Evans-type potential have further lengthened the semi-bonds; and this geometrical change has further reduced the non-bonding pressures on the bromine atoms by approximately as much as the stronger repulsions would have further increased them had the geometry remained unchanged.

Other trials which we have carried out with generally similar results involve retaining the exponential form of potential, but making it steeper or less steep by changing the length-constant in the exponent. However, we can give a single combined illustration of this and of another matter, which is considered in the next sub-section.

(d) *Angular Dependence of van der Waals Radii.*—As mentioned above, some doubt can be entertained as to whether these radii should be shortened at low angles to the bonding direction. Suppose that we decide not to shorten them. Then almost all compressions will be considerably strengthened; and we shall find appreciable non-bonding energy in the transition state of the reaction of the methyl group, and also in all initial states, including that of the reaction of the methyl group. The energy of steric hindrance of the reaction of a higher alkyl group will now have to be derived, without short-cuts, as the second difference of the total energies of four states, *e.g.*,

$$\left(W_{t\text{-Bu}}^{\text{transition}} - W_{\text{Me}}^{\text{transition}}\right) - \left(W_{t\text{-Bu}}^{\text{initial}} - W_{\text{Me}}^{\text{initial}}\right)$$

Since there are four terms, and in each extra compression can produce the sort of compensation already illustrated, the total opportunity for compensation is considerable.

In illustration we cite a calculation involving an exponential type of potential function, in which, not only have the compressions been intensified by omitting to shorten the van der Waals radii at low angles, but also they have been further strengthened by reducing the length-constant in the exponent, and thus steepening the exponential function. Instead of Born and Mayer's empirical constant 0.345 Å, we now assume the figure 0.165 Å, adopted by Westheimer (*loc. cit.*) to represent the properties of a function computed by Bleick and Mayer by a method of quantum-mechanical approximation for the mutual repulsion of two helium atoms (*J. Chem. Phys.*, 1934, 2, 252), Westheimer having employed this value in the potential function from which he derived hydrogen-bromine compression energies in the work cited above.† When using this potential function for computing hydrogen-bromine compressions, we set the energy zero at 3.15 Å, and when using it for carbon-bromine compressions, we change the minimum to 3.55 Å, these being the unreduced values of the respective van der Waals distances.

With these assumptions, the semi-bond length in the transition state of the methyl reaction becomes 2.55 Å: the steeper repulsive potential, and the greater range of repulsion, have lengthened it by 0.3 Å. The extra compression in the transition state of the *tert.*-butyl reaction lengthens it by a further 0.1 Å. The excess of total energy due to the presence of compression in the transition state of the *tert.*-butyl reaction is greater than the corresponding excess in the transition state of the methyl reaction by 5.4 kcal./mole. But the extra energy due to compression in the initial *tert.*-butyl bromide molecule exceeds that in the initial methyl bromide molecule by 2.7 kcal. mole⁻¹. It follows that the energy of steric hindrance of the *tert.*-butyl substitution is 2.7 kcal. mole⁻¹, in substantial agreement with the other estimates.

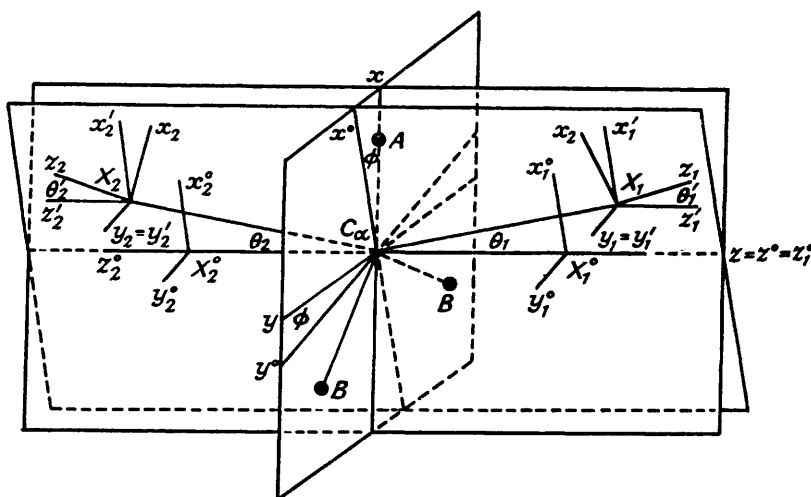
The general conclusion we draw from exploratory calculations such as have been illustrated, is that, in seeking to extend the work of Dostrovsky, Hughes, and Ingold, there is little to be gained from making changes in any of their assumptions of whose physical accuracy we are still uncertain, except the change which involves going over completely from the "stiff" to the "plastic" model.

* Corrected for the inconsistencies mentioned in the preceding footnote.

† We should not have assumed, however, that Born and Mayer's length constant, appropriate for compressions involving halide ions, would be applicable to the hydrogen-hydrogen repulsions discussed by Barton (*J.*, 1948, 340).

(B) METHODS OF CALCULATION.

In the energy calculations we have in principle, and in the entropy calculations in practice, to treat the transition and the initial states differentially. We must therefore adopt the "plastic" model for both states. In each, it permits every possible form of plasticity to the system of actually or potentially reacting atoms, but in the remainder of the alkyl groups it allows only conformational rotations, and not either bond-stretching or bond-bending. This model is, of course, a large advance on the "stiff" model; but it still involves the approximation of assuming that intra-alkyl deformation is not available to replace some of the non-bonding energy by a smaller amount of bonding energy; and of assuming also that, if the entropy associated with intra-alkyl vibrations is not negligible, at least the change which such entropy undergoes when a transition state is formed is negligible. This neglect of deformation in the alkyl groups, except at the reaction centre, is probably the biggest single source of error in the present work.

FIG. 1. *Co-ordinate system for transition states.*

(a) *Energy of the "Plastic" Model of the Transition and the Initial States.*—As regards the transition state, the main part of the energy problem is to calculate the total, bonding plus non-bonding, energy of the system of atoms concerned over a range of configurations, permitted by the model, and so chosen that it includes the configuration of the transition state. The calculation has not to be made absolute with respect to a physically prescribed zero, but in principle the zero of energy is that of the undeformed initial state. The first purpose for which this energy-configuration function is needed is in order to minimise it, thereby deriving both the geometry and the energy of the transition state. But the further purpose is to be kept in view of computing the entropy of the transition state, and this requires a knowledge, not only of its geometry, but also of the variation of its energy with configuration over a small range of configurations about that of the transition state.

The first proceeding is to choose axes fixed in the atomic assembly, and it is convenient to do this sufficiently comprehensively, as shown in Fig. 1, for use in all the steps of calculation mentioned. We shall have to describe both positions and displacements. For position axes, we take an origin at C_α , and the plane containing the three bonds from C_α to hydrogen or carbon as the xy -plane, one of the three bonds, the unique one if there is such, marking the x -axis: the directions of the y - and the z -axis then follow from the right-hand rule. The halogen atoms are assumed to lie symmetrically about the xy -plane. This will certainly be true for all transition states, except possibly those of the *isobutyl* group, for which we assume it nevertheless, because of the difficulty of making definite, and of working with, any other assumption. In the absence of non-bonding pressures,

the halogen atoms will lie on the z -axis, and certain resultant non-bonding pressures will leave them on that axis; but other resultant pressures will move them off this axis by some angle θ , leaving them still in the zx -plane; and yet others will shift them off that plane on to another derived from it by rotation about z by some angle ϕ . This rotation can be taken as defining new position axes, $x^\circ, y^\circ, z^\circ (= z)$; and the halogen positions can alternatively be expressed in polar co-ordinates r, θ, ϕ , having the usual relation to x, y, z . We require axes for the description of displacements of the halogen atoms, relatively to the rest of the atomic system, from their energy-minimised positions. For the general case, which it is always possible to specialise, we take them as lying in, or perpendicular to, the $z^\circ x^\circ$ -plane, but with origins at the halogens X_1 and X_2 . If we first set up for X_1 , displacement-axes x_1', y_1', z_1' , parallel to the position axes, and for X_2 a similar, but left-hand set, x_2', y_2', z_2' , derived from the X_1 -set by reflexion in the xy -plane, it is found that the normal displacements are rotated in the $z^\circ x^\circ$ -plane with respect to these axes by some angle θ' , and it is therefore convenient to take displacement co-ordinates in these rotated directions, $x_1, y_1 (= y_1'), z_1$ for X_1 , and $x_2, y_2 (= y_2'), z_2$ for X_2 .

The undeformed initial state is our energy zero, but we have to compute energies of deformation of the alkyl halide, first, as will be explained below, in connexion with the calculation of the excess of energy in the transition state, and, secondly, for the purpose of calculating the entropy of the initial state.

Axes set in the initial alkyl halide molecule are therefore chosen as shown in Fig. 2. For the description of position, the origin is at C_α , and the halogen X_1 lies on the z -axis. This defines an xy -plane, on which the three bonds from C_α to hydrogen or carbon can be projected, the projection of one of these bonds, the unique one if there is such, defining the x -axis, and the right-hand rule the y -axis. For the description of displacements of the halogen relatively to the alkyl group, axes $x_1, y_1, z_1 (= z)$, with an origin at X_1 , are taken parallel to the corresponding position axis.

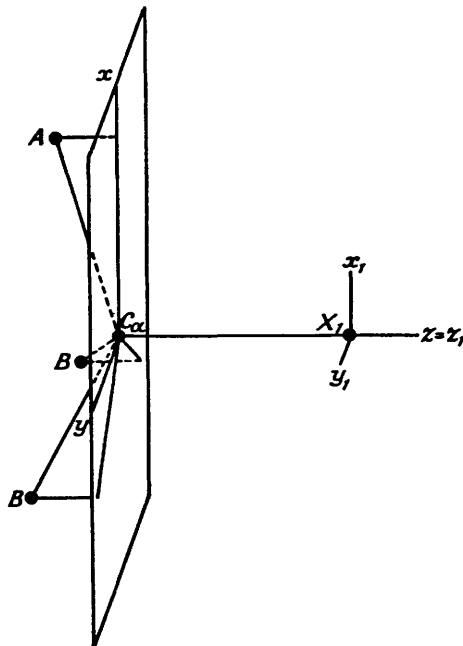


FIG. 2. Co-ordinate system for initial states.

The first step in the calculation of the energy-configuration function for the transition state is the simplifying one of determining, for each alkyl group, the angle ϕ : for the plane $z^\circ x^\circ$ thereby defined is to contain the halogens in the transition state, and hence a survey of the energy variation as the halogens move over this plane will provide a function, which, by minimisation, locates the transition state. In some cases it follows from symmetry that ϕ either may, or must, be taken as zero. In other cases ϕ can easily be determined, starting from the results which Dostrovsky, Hughes, and Ingold calculated with bromine as their halogen, or from similarly calculated results for chlorine and iodine. For it is essentially a question of finding the azimuth ϕ of the resultant non-bonding force on a halogen atom, initially placed on the z -axis at the point calculated by those authors, or by their method; and that, in turn, follows by vector summation of the individual atom-pair forces, which was computed by them for bromine, and may be similarly computed for chlorine and iodine. The correction which would allow for the curvature of the resultant force, as the halogen moves to its new position, turns out to be hardly worth making; and the results for chlorine, bromine, and iodine are so nearly identical that we can, with sufficient accuracy, adopt common values, as shown in Table 1.

In the problem of tracing the changes of total energy W over varying halogen co-ordinates in the $z^\circ x^\circ$ -plane, it is convenient to work at first in the polar co-ordinates r, θ .

For any particular pair of such co-ordinates, the procedure is to build up the configuration having them from the undeformed initial state in a series of steps, and to sum the corresponding energy changes. The energy of activation is thus described as the algebraic sum of eight terms, *viz.*, the energy needed (1) to bend the C-Br bond of the initial molecule from the z -direction through an angle θ assumed small, (2) to bend the other C_α bonds

TABLE 1. *Determination of the plane containing transition-state halogen.*

Alkyl group	Me	Et	Pr ^t	Bu ^t	Pr ⁿ	Bu ^t	<i>neo</i> Pe
Bond defining x	$C_\alpha H_\alpha$	$C_\alpha C_\beta$	$C_\alpha H_\alpha$	$C_\alpha C_\beta$	$C_\alpha C_\beta$	$C_\alpha C_\beta$	$C_\alpha C_\beta$
Angle ϕ	0°	11°	0°	0°	11°	0°	21°

into the xy -plane, (3) to remove enough solvent sufficiently far from the reacting particles to permit their interaction, (4) to force the halide ion against the α -carbon atom at the angle θ , and to the separation r , (5) to stretch the C-Br bond to the length r , (6) to divide the ionic charge between the halogen atoms, (7) to release any non-bonding pressures in the initial state, and (8) to do the necessary work against such pressures exerted on the halogen atoms in the (r, θ) -configuration by all other atoms in the system except the α -carbon atom. The terms (6) and (7) are negative, and the other terms positive. The simplifying assumptions made are that energy (1) is controlled by a simple harmonic potential for the small angles θ involved, that energies (2) and (3) can be treated as independent of r and θ , as also can (6) for configurations near that of the transition state, about which this term must pass through a stationary value, that energies (4) and (5) may be treated as dependent on r , but not on θ for the small angles considered, although energies (7) and (8) must be computed as functions jointly of r and θ . The constant terms (2), (3), and (6) need not be calculated explicitly, since they will always cancel in the energy differences with which we shall be concerned, *viz.*, (a) the extra energy conferred on undeformed transition states by increased non-bonding compressions, directly, and through their effect on configuration and hence on bonding energy, and (b) the further energy which transition states acquire by deformation. It remains to compute the configuration-dependent terms for a suitable (r, θ) -manifold, *viz.*, terms (1), (4), (5), and (8), as well as the initial-state-dependent term (7).

Except for energy term (1), which is a new feature in these calculations, all the necessary formulæ are in the paper of Dostrovsky, Hughes, and Ingold, who also cited the sources of the atomic and bond constants needed for their application. The constants, which we have taken from the same sources, except for some revised frequencies, the source of which is mentioned later, are in Table 2. The non-bonding energy formulæ contain

TABLE 2. *Adopted atomic and bond constants.*

Z	[R] (cm. ³ mole ⁻¹)	\mathcal{J} (ev)	ρ_w (Å)	D (CZ) (kcal. mole ⁻¹)	ν (CZ) (cm. ⁻¹)	r_0 (Å)
C	2.41	12.0	1.6	—	—	1.54
H	1.09	14.5	1.2	—	—	1.09
Cl	5.9	12.2	1.8	80	732	1.76
Br	8.8	10.5	1.95	67	611	1.91
I	13.7	9.5	2.15	53	533	2.10
Cl ⁻	8.7	9.5	1.81	—	—	—
Br ⁻	12.2	9.0	1.95	—	—	—
I ⁻	18.5	8.7	2.16	—	—	—

the polarisability α , and the ionisation potential \mathcal{J} , of the atoms concerned, the former following from the refraction constant R by multiplication by $3/4\pi N$. For the ionisation potential of the iodide ion, we had no direct source, and the figure entered in the Table is the one we assumed, after a survey of other values applying to bound and ionised halogens. For the polarisabilities and ionisation potentials of semi-bound semi-ionic halogens, we took means between corresponding values for the bound halogen atoms and the halide ions. The non-bonding energies also depend on the effective van der Waals radii ρ_w of the atoms involved, and, for obtuse angles χ to the bond direction, these were taken equal to the maximum radii ρ_w given in the Table, but for acute angles were reduced from these maxima by $0.4(1 + \cos 2\chi)$ or $0.2(1 + \cos 2\chi)$ Å, as already explained. The bonding-energy formula contains the dissociation energy D , the stretching frequency ν , and the length

r_0 of the bond. For the first two of these quantities, we took methyl halide values, because the Morse formula used is designed for application to diatomic molecules, and the methyl halides are the only alkyl halides in which the halogen-stretching vibrations are sufficiently free from intramolecular coupling to permit of treatment on this basis, which we have to make self-consistent.

Of the many bending potential functions V which might have been employed for the calculation of the energy term (1), the simplest is that given by Cross and van Vleck (*J. Chem. Phys.*, 1933, **1**, 356) as a result of their valency-force treatment of the vibrations of ethyl chloride, bromide, and iodide. For here, the total energy associated with the bending of a CCHal-angle is expressed as a function of the change $\Delta\gamma_C$ in that angle only, although other valency angles must change with it for obvious geometrical reasons :

$$2V = K_C(\rho^2_{CO} + \rho^2_{CHal})\Delta\gamma_C^2$$

The values of K_C , the bending force-constant, are in Table 3. We have used this function whenever possible, *i.e.*, except for methyl halides, y -bending in primary alkyl halides, and x -bending in the *isopropyl* halides (see Figs. 1 and 2). For these deformations, we require energy as a function of the change $\Delta\gamma_H$ of HCHal-angles, and for this we took the square-term part of the bending-potential function of Crawford and Brinkley (*J. Chem. Phys.*, 1941, **9**, 69). In this function, which may be expressed in the form,

$$2V = k_H(\rho^2_{CH} + \rho^2_{CHal}) \Sigma\Delta\gamma_H^2$$

all the geometrically related angular changes are considered to make their own contributions to the energy of deformation, and the bending force-constant k_H applies to each such change, so that a sum must be taken. The values of k_H are in Table 3. The application of this equation to the methyl halides is straightforward, but its application to y -bending in primary alkyl halides, and to x -bending in *isopropyl* halides, involves the approximation of assuming that, in these deformations, the CCHal-angles, the changes in which are small relatively to the changes in the HCHal-angles, so that they contribute but little to the energy, can with sufficient accuracy be treated as though they were HCHal-angles.

TABLE 3. *Adopted values of bond-bending force-constants.*

	RCl	RBr	RI
$10^6 K_C$ (with K_C in dyne cm. ⁻¹)	0.22	0.22	0.18
$10^6 k_H$,, k_H ,,	0.16	0.13	0.10

For each point r , θ in the selected manifold of each of the 21 reactions considered (7 alkyl groups and 3 halogens), the calculation described has been carried through, but only with respect to the configuration-dependent energy terms (1), (4), (5), and (8); because the inclusion of the initial-state term (7) in the programme is a formality. For Dostrovsky, Hughes, and Ingold showed that, by the method of calculation which they used, the compression energy in all initial states is either zero, or, when compared with the compression energy of corresponding transition states, is too small to be worth taking into account. The present extension of their method cannot change that conclusion. So, for each reaction, the energies (1), (4), (5), and (8), calculated for each r , θ , are added, and the totals are plotted as a surface over the co-ordinate plane $r^2\theta^2$. Each surface has the form of a basin, the lowest point in which gives the configuration and energy of the transition state.

These results are illustrated and tabulated in Section C, where also they are discussed in relation to kinetic observations.

(b) *Entropy of the "Plastic" Model of the Transition and the Initial State.*—In the transition-state theory, reaction rate depends on the proportion of molecular systems maintained in the transition state, and therefore, not only on the energy difference between the initial and the transition state, but also on the ratio of their statistical probabilities of occupation, and thus on its logarithm, the entropy difference. For any overall state, the probability is given by a Boltzmann-weighted count of the individual energy-states included in it, the weighting factor making lower-lying energy-states more important in

the count. We shall assume that the total wave-function can be so factorised that each vibrational state carries with it a similar set of rotational states, each of which in turn carries a similar set of translational states, the total number of energy states being therefore the product of the numbers of vibrationally, rotationally, and translationally, distinctive kinds of states, and the total entropy the sum of the vibrational, rotational, and translational entropies. We have to deal with reaction in solution, and shall assume further that the transition state, and each species composing the initial state, behave as ideal solutes. And on this basis we shall calculate, for the adopted model, the entropies of the transition and initial states, at a standard concentration, 0.0446M, and a standard temperature, 298.1°K. The particular standard of concentration chosen (which corresponds to an ideal osmotic pressure of 1 atmosphere) is of no importance: at another concentration, all the calculated entropies would be changed by a constant amount, and so the differences, in which alone we are interested, would be unaltered. The adopted temperature is within the general range of our experimental investigations: a change to another temperature would produce non-uniform changes in the entropies; but the effect on the entropy differences of a change to another temperature within our range would be quite small.

The formula for translational entropy derives from the quantal theorem of the particle-in-a-box, and the only molecular quantity involved is the mass of the particle, heavier particles having more low-lying energy levels than lighter. For our purposes the equation may be reduced to the form,

$$S_i = 2.303R(1.5 \log M + 2.5 \log T) - 2.315$$

cal. deg.⁻¹ mole⁻¹, at the standard concentration, or

$$S_i = 2.303R(1.5 \log M) + 0.515$$

cal. deg.⁻¹ mole⁻¹, at the standard concentration and temperature. Here the constant term is so adjusted that the mass M is simply the chemical molecular weight.*

At once we see a factor which will tend to make higher homologues react more slowly, independently of the position of the extra mass in the higher homologue, and therefore independently of any question of steric hindrance. The entropy of activation S^\ddagger is the entropy S of the transition state XXR^- , minus the sum of the entropies S of the components RX and X^- of the initial state; † so that for the translational contribution, we have

$$S_i^\ddagger = S_i(XXR^-) - [S_i(RX) + S_i(X^-)]$$

The translational entropy of X^- is, of course, constant from one alkyl group to another. However, in a higher homologue, the masses of XXR^- and of RX are increased by the same amount; and so, because the former mass is larger to start with, it will be increased in smaller ratio than will the latter; and since, for the entropy, it is the logarithm of the mass that matters, $S_i(XXR^-)$ will be increased less than will $S_i(RX)$, with the result that the translational entropy of activation S_i^\ddagger will be lowered.

The calculation of rotational entropies is derived from the quantal problem of the rotor, the energy levels of which are lowered and concentrated by increasing the moments of inertia, though some energy states may disappear when symmetry causes certain rotations to make no physical difference. For our purposes the equation may be reduced to

$$S_r = 2.303R(0.5 \log ABC - \log \sigma + 1.5 \log T) - 5.384$$

cal. deg.⁻¹ mole⁻¹, or, at the standard temperature,

$$S_r = 2.303R(0.5 \log ABC - \log \sigma) - 3.686$$

* Here and later, constant terms in expressions for entropy are calculated with Birge's 1939 values of the universal constants, k , h , and N .

† For convenience in this paper, we simplify the standard symbols ΔS^\ddagger and ΔH^\ddagger , down to S^\ddagger and H^\ddagger , for entropy and heat of activation, thus allowing ‡ to be, not only the label of a process, but also the operator which takes a difference over it. This is because we have needed Δ as the operator for taking another kind of difference, that which attends the replacement of methyl by a higher alkyl group. We are concerned with both kinds of first difference, *e.g.*, ΔS and S^\ddagger , as well as second differences, *e.g.*, ΔS^\ddagger , which in our equations signifies the constitutional increment in the entropy of activation.

cal. deg.⁻¹ mole⁻¹. Here A , B , and C are the principal moments of inertia, σ is a symmetry factor, and the value of the constant term is so fixed that A , B , and C are to be calculated in atomic-weight-square-Ångström units.

We find here a constitutional effect on rotational entropy, and hence on entropy of activation, and on reaction rate, which, even though it depends on the position of an added mass, is not an effect of steric hindrance, though, still more easily than the translational entropy effect, it might be mistaken for such. The rotational entropy of activation is given by the difference

$$S_r^\ddagger = S_r(\text{XRX}^-) - S_r(\text{RX})$$

since the rotational entropy of the halide ion may be taken as zero. This part of the entropy of activation is always positive, because the mass added to the original molecule in the formation of the transition state must increase at least one, and cannot decrease any, moment of inertia, and any disturbance due to symmetry, even if non-uniform, will be too small to make a difference. Now we can show that an inert mass, added to the original molecule by a structural change, may either increase or decrease the rotational entropy of activation, according as the added mass is sufficiently far away from, or sufficiently near to, the reaction centre. The reason for the positional distinction is that, in the former case, the centre of gravity moves away from, and, in the latter, it moves towards, the point at which mass is being increased in the formation of the transition state.

A formal proof could be given, but is intricate, and a simple numerical illustration is easier to follow. Let the original molecule be represented by two unit masses, A and B , unit distance apart, A being the reaction centre; then its moment of inertia will be $1/2$. Let a transition state be formed by the addition of a reagent of unit mass at A ; then its moment of inertia will be $2/3$, a proportional increase of $4/3$, so that the rotational entropy of activation, except for a constant term, will be proportional to $\log 1.33$. Now suppose that we add to the original molecule another unit of mass at B ; then the moment of inertia of the molecule will become $2/3$, and that of the transition state $4/4$, a proportional increase of $3/2$, so that the rotational entropy of activation, apart from the constant term, will be proportional to $\log 1.5$, *i.e.*, it will be larger than before. But suppose that, instead of adding the extra mass at B , we had added it at A ; then the moment of inertia of the molecule would still be $2/3$, but that of the transition state would be $3/4$, a proportional increase of $9/8$, so that entropy of activation, except for its constant part, would be proportional to $\log 1.125$, *i.e.*, less than if the extra mass had been added at B , and even less than if it had not been added at all.

In purely aliphatic molecules, the simple distinction illustrated is subject to a bias in favour of the effects expected from substitution near the reaction centre, because of the non-linearity of the carbon chains. We have now three moments of inertia to take into account: even an ω -extension of a non-acetylenic chain is usually not far enough away from any principal axis of inertia to produce a positive differential, from the initial to the transition state, in the factors of increase of the corresponding moment of inertia, which can counteract the effect of the proximity of the extension to another principal axis in producing a negative differential in the factor of increase of another moment of inertia. The result is that even ω -extension will usually decrease the rotational entropy of activation, whilst α -branching will decrease it more strongly. Thus the general effect of rotational entropy, like that of translational entropy, is in the direction of making higher homologues react more slowly; and rotational entropy has the further peculiarity that its retarding influence comes out most strongly with α -branching, just as if the effect were one of steric hindrance; with which it has actually nothing to do, since any bulk that might be associated with the added mass has not yet been taken into account. Isotopic substitution by a heavier isotope at different points along the carbon chain, where there would be a mass change without a volume change, would show the effect described.

Our calculations of rotational entropy involve some approximations arising from the model employed, a simplified one, which allows for conformational rotation, but not for bond-stretching and -bending, within the alkyl groups. We have therefore assumed that

conformational rotation will combine with overall rotation in the relevant region of temperature, and have calculated symmetry numbers accordingly. In the cases of the *n*-propyl and *isobutyl* halides, we were in the difficulty of not knowing which conformations are predominant, and to what extent. We decided that the procedure which would be most faithful to the model, and would at the same time act as an insurance against an error of the magnitude which might be incurred through the assumption of a wrong conformation, would be to calculate, in each such case, entropies for all conformations, and take the average. There are, of course, three, the *anti*-, and the *D*- and *L*-*syn*-conformations, designated always with reference to the unique groups attached to the β - and the α -carbon atom. Since the calculations here reported were finished, Brown and Sheppard have shown spectroscopically (*Trans. Faraday Soc.*, 1954, 50, 1164) that both *anti*- and *syn*-conformations are present in comparable amounts in liquid *n*-propyl chloride, bromide, and iodide, and in *isobutyl* chloride. But we still do not know the proportions, though it seems fairly certain that in liquid *isobutyl* chloride the *syn*-conformation is in distinct excess, perhaps an excess not far removed from the 2:1 excess which our calculations assume.

The calculation of vibrational entropy proceeds from the quantal problem of the harmonic oscillator. Normal vibrations being, by definition, independent of each other, the total number of vibrational energy levels is the product of the numbers of those of each normal vibration; and thus, each of the $3n-6$ normal vibrations of an *n*-atomic non-linear molecule, or the $3m-7$ vibrations of an *m*-atomic transition state, makes its own contribution to the vibrational entropy, so that a sum has to be taken. The lower a fundamental frequency, the more concentrated will be the energy levels of its vibration, and the greater will be the entropy contribution of the latter. The formula for vibrational entropy is

$$S_v = \sum_{\text{vibs.}} [-R \ln (1 - e^{-x}) + Rxe^{-x}/(1 - e^{-x})]$$

where $x = h\nu/kT$, ν being the vibration frequency in sec^{-1} . At our standard temperature, $x = 0.00483\omega$, where ω is the vibration frequency in cm^{-1} .

Our model involves the assumption that all intra-alkyl vibrations are large enough to be unexcited, so that their entropy contribution is zero in both the transition and the initial state, leading to a difference of zero, as their contribution to the vibrational entropy of activation. Of course, the vanishing individual entropies are unrealistic; but we hope that intra-alkyl vibrations will make such similar contributions to the vibrational entropy in the transition and the initial state that the differences of these contributions, if not zero, will be small, and, what is more important to us, the differences between these differences, from case to case, will be quite small.

The serious part of our calculation of vibrational entropies is therefore that concerned with the actual or potential reaction centres. We have to determine the fundamental frequencies of the systems of atoms concerned. In the transition state, the system has 5 vibrations, whose normal co-ordinates are sufficiently distinguished by the displacements of the halogen atoms (see Fig. 1). They are $z_s = z_1 + z_2$, $x_s = x_1 + x_2$, $y_s = y_1 + y_2$, $x_a = x_1 - x_2$, and $y_a = y_1 - y_2$, the sixth degree of freedom of the two halogen atoms, $z_1 - z_2$, being the reaction co-ordinate. The subscripts *s* and *a* signify that the first three vibrations are symmetric to the *xy*-plane, and that the last two are antisymmetric. In all five vibrations, the alkyl group undergoes translatory oscillations, if, and to the extent to which, this is necessary in order to hold still the centre of gravity; and in the last two vibrations it undergoes librations to the extent required to conserve angular momentum. In the trigonal transition states of the methyl and *tert.*-butyl groups, the vibrations x_s and y_s form a degenerate pair (Π_u , to the spectroscopist), and x_a and y_a form another such pair (Π_g , in his language). The other transition states involve no such degeneracies. In the trigonal transition states, the non-degenerate vibrations and the degenerate pairs belong to three different symmetry species. In the other transition states, there are four symmetry species, because z_s and x_s fall into the same species, while each of the other vibrations has its own species. The occurrence of two non-degenerate vibrations in the same species has

the consequence that their frequencies appear as the solutions of a quadratic equation, without any accompanying mathematical instruction for distributing the roots between the two normal co-ordinates.

Corresponding to these five vibrations of the transition state, and to the translational motion in the reaction path, the initial state will have three degrees of freedom of translation of the halide ion, with which we are not now concerned, together with three vibrations of the bound halogen atom relatively to its alkyl group. These vibrations may be distinguished by the displacement co-ordinates of the halogen atom (see Fig. 2), as z_1 , x_1 , and y_1 . In the trigonal halides of methyl and *tert.*-butyl, the vibrations x_1 and y_1 form a degenerate pair (E , to the spectroscopist). In the other alkyl halides, all vibrations are non-degenerate. In all alkyl halides, each non-degenerate vibration, and each degenerate pair, has its own distinct species.

Reverting to the transition state, the starting point of our determination of its vibration frequencies, and thus of the vibration entropy, consists in the basin-shaped energy surfaces, calculated as described in the preceding sub-section. The limiting directions of the principal axes of the lowest contours of such a surface give the directions of the displacements, z_1 , x_1 , etc. (see Fig. 1), *i.e.*, they determine the angle θ' , which is not the same as θ , unless both are zero. Sections of the surface, cut along these directions, yield curves, whose lowest portions, when approximated to parabolæ, give force-constants for the displacements z_1 , x_1 , etc., and hence the force-constant for the vibration z_s , and the bending force-constant of the two vibrations x_s and x_a . The bending force-constant we prefer to handle as a moment-constant, into which it may be converted by multiplication by the square of the distance of a halogen atom from the centre of its rotatory motion in the bending vibration concerned. We have not a sufficient background of energetic information systematically to compute the moment-constant governing the other two vibrations y_s and y_a . But for the methyl and *tert.*-butyl transition states, we know, from the trigonal symmetry, that this moment-constant will be exactly equal to the previous one; and for the other transition states we can make approximate estimates. Our estimates are based on the assumption that the moment-constant relevant to the vibrations y_s and y_a will be determined mainly by those attachments to C_α which have extension in the y -direction, *i.e.*, the system $BC_\alpha B$ in Fig. 1. Therefore, for the transition states of all primary alkyl groups, we take this moment-constant as equal to that of the transition state of the methyl group; and for the transition state of the *isopropyl* group, we take it as equal to the moment-constant of the transition state of the *tert.*-butyl group. Since the moment-constants of the transition states of the methyl and *tert.*-butyl groups differ by only 7%, so that their square roots, to which frequencies are proportional, differ by only 3.5%, it would seem probable that no large error is here involved.

The calculation of mass-factors for the frequency formulæ is a mechanical matter, except for the vibrations y_s and y_a of those transition states in which both hydrogen and carbon atoms are bound to C_α . Here, as already explained, we cannot follow logically the requirements of the model; and, since we cannot, it seems best to make the simplest available, reasonably realistic, approximations. For y_s in these cases, we assume that most of the oscillatory motion of the alkyl group will be centred in the α -carbon atom, which will carry its attached hydrogen atoms with it, leaving the heavier carbon attachments only negligibly disturbed. For y_a in the same cases, we assume that the libratory alkyl motion is concentrated in the $BC_\alpha B$ -group (Fig. 1), and is so nearly pivoted about the $C_\alpha A$ -bond, that the rest of the alkyl group is negligibly disturbed.

With these approximations, frequency formulæ for the transition states have been developed, which are of valency-field type, without cross-terms. It is to be noted that the so-called valency forces have to be taken along z_1 and z_2 , and are therefore not centred at C_α , unless $\theta' = \theta$, which is never true, except when both are zero. Let f_z be the force constant for the vibration z_s in dyne cm^{-1} , and let Δ_x be the moment-constant for the vibrations x_s and x_a , and Δ_y that for the vibrations y_s and y_a , in dyne $\text{cm} \cdot \text{radian}^{-1}$. Let M , M_h , M_a , M_m , and M_p be the chemical molecular weights of the transition state, a halogen atom, the alkyl group, a methylene group, and a methine group, respectively. Let I_x , I_{hx} , I_{ax} , I_{mx} , and I_{px} be the moments of inertia, in atomic-weight-square-Ångström

units, of the transition state, a halogen atom, the alkyl group, the α -methylene group, and the α -isopropylidene group, respectively, about an axis parallel to x_0 through the centre of gravity of the transition state; and let I_y , I_{hy} , and I_{ay} , have corresponding meanings in relation to an axis parallel to y_0 , through the centre of gravity. Let r_t be the length of a halogen semi-bond in Å. When $\Delta_x = \Delta_y$, $I_x = I_y$, $I_{hx} = I_{hy}$, or $I_{ax} = I_{ay}$, we shall write either of the equal quantities as Δ_{xy} , I_{xy} , I_{hxy} , or I_{axy} , as the case may be. If c is the velocity of light, and if ω_{zs} , ω_{xs} , ω_{ys} , ω_{za} , and ω_{ya} are the frequencies in cm^{-1} of the vibrations z_s , x_s , y_s , x_a , and y_a , respectively, the formulæ giving these frequencies in the various transition states are as follows. For the methyl and *tert.*-butyl transition states, they are

$$\begin{aligned} 4\pi^2 c^2 \omega_{zs}^2 &= 2f_z N / M_h \\ 4\pi^2 c^2 \omega_{xs}^2 &= 4\pi^2 c^2 \omega_{ys}^2 = 2\Delta_{xy} M N / 10^{-16} M_h M_a r_t^2 \\ 4\pi^2 c^2 \omega_{xa}^2 &= 4\pi^2 c^2 \omega_{ya}^2 = \frac{1}{2} \Delta_{xy} I_{xy} N / 10^{-16} I_{hxy} I_{axy} \end{aligned}$$

For the ethyl, *isopropyl*, *n*-propyl, *isobutyl*, and *neopentyl* transition states, the formulæ are

$$\begin{aligned} 4\pi^2 c^2 \omega_{zs}^2 + 4\pi^2 c^2 \omega_{xs}^2 &= \frac{f_z N}{M_h} \left(1 + 2 \frac{M_h}{M_a} \sin^2 \theta' \right) + \frac{2\Delta_r N \cos^2 \theta'}{10^{-16} M_h r_t^2 \cos^2 \theta} \left(1 + 2 \frac{M_h}{M_a} \cos^2 \theta' \right) \\ 4\pi^2 c^2 \omega_{zs}^2 \cdot 4\pi^2 c^2 \omega_{xs}^2 &= 2f_z \Delta_x M N^2 \cos^2 \theta' / 10^{-16} M_h^2 M_a r_t^2 \cos^2 \theta \\ 4\pi^2 c^2 \omega_{ys}^2 &= 2\Delta_y (2M_h + M_m) N / 10^{-16} M_h M_m r_t^2 && \text{(not isopropyl)} \\ ,, &= 2\Delta_y (2M_h + M_p) N / 10^{-16} M_h M_p r_t^2 && \text{(isopropyl)} \\ 4\pi^2 c^2 \omega_{xa}^2 &= \frac{1}{2} \Delta_x I_y N / 10^{-16} I_{hy} I_{ay} \\ 4\pi^2 c^2 \omega_{ya}^2 &= \frac{1}{2} \Delta_y (2I_{hx} + I_{mx}) N / 10^{-16} I_{hx} I_{mx} && \text{(not isopropyl)} \\ ,, &= \frac{1}{2} \Delta_y (2I_{hx} + I_{px}) N / 10^{-16} I_{hx} I_{px} && \text{(isopropyl)} \end{aligned}$$

Consistently with our model, we have calculated initial-state halogen frequencies under the assumption that the alkyl groups behave as vibrationless assemblies. This was in order to obtain vibrational entropies comparable with those similarly calculated for the transition states, so that errors due to non-rigidity in the alkyl groups, and consequent coupling between halogen and alkyl vibrations, would be largely self-compensatory in the differences representing vibrational entropies of activation.

As a basis of force-constants for halogen-stretching vibrations z_1 (cf. Fig. 2), we have used the observed, and securely assigned, halogen-stretching frequencies of the methyl halides, which cannot be disturbed by halogen-bending; and we have applied these force-constants to z_1 vibrations throughout. As source of the moment-constants for halogen-bending against hydrogen, we have taken the observed, and definitely assigned, halogen-bending frequencies of the methyl halides, which cannot be disturbed by halogen-stretching; and these moment-constants we have applied to all halogen-bending vibrations in which the main angular change is in HCHal-angles, *i.e.*, to the y_1 vibrations of all primary halides, and to the x_1 vibrations of *isopropyl* halides (cf. Fig. 2). As source of the moment-constants for halogen bending against carbon, we have used the observed, and equally well assigned, low bending frequencies of the ethyl halides, Cross and van Vleck's investigation having shown that these frequencies are very little disturbed by halogen stretching; and we have applied these moment constants to all halogen-bending vibrations in which the main angular change is in CCHal-angles, *i.e.*, to the x_1 vibrations of all primary alkyl halides, the y_1 vibrations of *isopropyl* halides, and the x_1 and y_1 vibrations of *tert.*-butyl halides.

For the derivation of force- and moment-constants of the initial state, we have chosen as our observational basis the frequencies of the methyl and ethyl halides, not only because these are the simplest sources to which we could have turned, but also because their use

is demanded by the requirement of consistency with our treatment of the vibrations of the transition state; for these same frequencies were employed, in Morse or harmonic functions, during the construction of the transition-state energy surfaces, and they are therefore at the basis of the force- and moment-constants, therefrom computed, by means of which the transition-state frequencies were calculated.

In the following frequency formulæ, we write f_z for the force-constant in dyne cm^{-1} for the vibration z_1 , and Δ_x and Δ_y for the moment-constants in dyne cm. radian^{-1} for the vibrations x_1 and y_1 respectively. We also write M , M_h , and M_a for the chemical molecular weights of the alkyl halide, the halogen atom, and the alkyl group, respectively, I_x , I_{hx} , and I_{ax} for the moments of inertia in atomic-weight-square-Ångström units of the same respective systems about an axis parallel to x through the centre of gravity of the alkyl halide, and I_y , I_{hy} , and I_{ay} for the corresponding moments of inertia about an axis parallel to y through the centre of gravity. When $\Delta_x = \Delta_y$, $I_x = I_y$, $I_{hx} = I_{hy}$, or $I_{ax} = I_{ay}$, we shall write Δ_{xy} , I_{xy} , I_{hxy} , or I_{axy} for either of the equal quantities. The frequencies, in cm^{-1} , of the vibrations z_1 , x_1 , and y_1 , denoted by ω_z , ω_x , and ω_y respectively, are given, for methyl and *tert.*-butyl halides, by the formulæ

$$4\pi^2 c^2 \omega_z^2 = f_z MN / M_h M_a$$

$$4\pi^2 c^2 \omega_x^2 = 4\pi^2 c^2 \omega_y^2 = \Delta_{xy} I_{xy} N / 10^{-16} I_{hxy} I_{axy}$$

and, for ethyl, *isopropyl*, *n-propyl*, *isobutyl*, and *neopentyl* halides, they are given by the equations

$$4\pi^2 c^2 \omega_z^2 = f_z MN / M_h M_a$$

$$4\pi^2 c^2 \omega_x^2 = \Delta_x I_y N / 10^{-16} I_{hy} I_{ay}$$

$$4\pi^2 c^2 \omega_y^2 = \Delta_y I_x N / 10^{-16} I_{hx} I_{ax}$$

Let us now extract, as we did from the formulæ for translational and rotational entropy, what the present formulæ for vibrational entropy teach of general principle concerning constitutional effects on entropy of activation. We shall find in vibrational entropy a more complicated situation than was encountered before, inasmuch as, now, both accelerating and retarding factors are present, which do not depend on steric hindrance, and also real steric effects, which themselves may be either accelerating or retarding.

The vibrational entropy of activation is given by the difference

$$S_v^\ddagger = S'_v(\text{XRX}^-) - S_v(\text{RX})$$

since $S_v(\text{X}^-) = 0$. (The dash in the symbol for the transition-state term is added as a reminder that a transition state has one vibration less than it would have if it were a molecule.) The vibrational-entropy formula shows that vibrational entropies rise as frequencies fall. The frequency formulæ contain both masses and moments of inertia, always to a higher power in the denominator than in the numerator, and often in the form of a sum divided by the product of its parts. These formulæ therefore show that the general effect of an added mass, as on proceeding to a higher homologue, will be to lower frequencies and raise vibrational entropies, but to do these things less strongly in the transition state than in the initial state, because the mass and moments of inertia of the former are larger, and so the changes they suffer are proportionally smaller.* On this count, an added mass will reduce vibrational entropy of activation, and to that extent reaction rate. On the other hand, there are a larger number of frequencies to be lowered, and their entropy contributions raised, by an added mass in the transition state, than in the initial state. For this reason, an added mass could raise vibrational entropy of activation, and hence the

* The asymptotically logarithmic relation of frequency to entropy follows by expanding the summand of S_v in the series

$$R(-\ln x + 1 + x^2/24 + \text{higher-power terms})$$

which converges with increasing rapidity as $x = h\nu/kT$ becomes smaller.

frequency of reaction rate. Moreover, for reasons similar to those considered in connexion with rotational entropy, stronger rate-depressing effects on the first count, and stronger rate-enhancing effects on the second, may arise in the group of vibrations which depend on moments of inertia, when the extra mass is added nearer the reaction centre. Finally, our formulæ make some allowance for the circumstance that all parts of an alkyl group are not equally coupled to the motion of the halogens. The summing-up of this situation is involved in its detail, but it can be shown to yield the conclusion that, in a purely aliphatic system such as ours, an added mass will in general reduce the vibrational entropy of activation, but that a sufficient loading with extra masses near the reaction centre may increase it. Of course, neither the implied general retarding effect, nor the more specialised accelerating effect on the frequency factor of reaction rate, is of steric origin, since it would be the same if the added mass had no bulk. Indeed, if we were discussing isotopic substitution by a heavier isotope there would be nothing more to say.

But vibrational frequencies depend, not only on mass factors, but also on force-constants; and it is here that steric hindrance can come in quite genuinely, though not always with the effects we might have expected. It is sufficient to think now only of the transition state, in which the main steric pressures occur. The force-constants which control the vibrations of the reacting atoms in the transition state are determined by the narrowness and depth of the potential hollow, the bottom of which is occupied by the configuration of the transition state. The effect of steric pressure is to "push" this potential well either outwards or sideways, or in both ways; and, as to the influence of such displacements on the shape of the well, all will depend on whether it is displaced against a steepening energy cliff, or into a region of gentler energy gradients. If the displacement is outwards, and so into a region where a Morse curve would begin to curl over, the energy hollow will become shallower in that direction, as is already illustrated in Dostrovsky, Hughes, and Ingold's paper by their Fig. 6; and if such outward displacement were to relieve lateral steric pressure, then the hollow would become shallower laterally. In any case, increased proximity to the lip in the energy surface, which occurs further out than the transition state, will lead to smaller force-constants, lower frequencies, and more vibrational entropy in the transition state, and therefore to a higher vibrational entropy of activation, and to a steric enhancement of the frequency factor of reaction rate. But, to take another case, suppose that the steric displacement of the energy hollow is sideways, against the steepening wall of an essentially harmonic bending potential. Then the hollow will be narrowed, the force-constants and frequencies will be increased, and the vibrational entropy of activation will be reduced; so that, for this steric reason, the frequency factor of reaction rate will be diminished.

It seems correct to apply the term "non-steric" to that part of the effect of added masses which depends on their position but not on their volume, because the word "steric" implies a space-filling quality, and comes from a root meaning "solid." It may be convenient to have a collective (and positive) name for those non-polar, non-steric, entropy effects which depend on mass, including its position, but without bulk and without charge: such effects could be called "ponderal" entropy effects, since they follow from the mechanics of mass-points.* We can then distinguish three possible kinds of entropic effects of structure on reaction rate (and equally on reaction equilibria), *viz.*, ponderal, steric, and polar. (It is only because the present study of structural effects is restricted to alkyl groups that we shall have hardly any concern in this paper with polar entropic effects.)

In our numerical calculations of vibrational entropy, we met the difficulty, already encountered in the calculations of rotational entropy, that, in the cases of *n*-propyl and isobutyl halides, we do not know the proportions in which the conformations occur. Here, as before, we pursued the routine of calculating for all conformations, and accepting the average of the resulting entropies.

The numerical data used in the entropy calculations described, apart from those on which the energy surfaces are based, consist only of some vibration frequencies, as noted

* After consultation with the Editor, the established word "ponderal" (definition: pertaining to weight) has been adopted. Its meaning is clearly different from that of "ponderous" (definition: having great weight).

in Table 4. Those for the methyl halides are from the work of Bennett and Meyer, Barker and Plyler, and Noether, as collated by Herzberg ("Infra-red and Raman Spectra," van Nostrand, New York, 1945, p. 315), and those for the ethyl halides are values cited by Kohlrausch ("Der Smekal-Raman-Effekt," Springer, Berlin, 1938, Ergänzungsband, p. 133), as being derived from various consistent observations of Raman spectra; and they are among the values used by Cross and van Vleck (*loc. cit.*) for computing one of the types of force-constant which we have employed in the construction of our energy surfaces.

TABLE 4. *Adopted basic frequencies (in cm.⁻¹).*

RX	RCI	RBr	RI
MeX (CX-stretching)	732	611	533
MeX (HCX-bending)	1015	952	880
EtX (CCX-bending)	335	292	262

Our reactions occur in solution, and therefore one further type of contribution to the entropies of the initial and transition states must be considered, *viz.*, entropy of solvation. The entropy of solvation of the halide ion in the initial state will be a large negative quantity, because the central charge will cut away some translational and rotational entropy from the nearer solvent molecules; but it will always be the same, and will therefore appear only as part of an unevaluated constant term in the entropies of activation, and will disappear from their differences, which are all that we compare with experiment. Solvation being a local matter, we can consider the entropy of solvation of the transition state in two parts. By far the most important is the entropy of solvation of the pair of halogen atoms, each bearing half the total anionic charge, and we may, if we choose, take in the carbon atom between them. This entropy term will also be large and negative; but it too will be the same in all cases, and so will come into the constant term of the entropy of activation, and will disappear from the differences with which we are concerned. Similarly, we can divide the solvation entropies of the alkyl halide molecules into two parts, and consider first the part dependent on the dipolar CHal-group. This will be almost the same from case to case, and so will provide another, though relatively small, contribution to the constant term in the entropy of activation, and, once again, will disappear from the differences. There remain the solvation entropies of the rest of the alkyl group in the transition state, and of the rest of it in the initial state. These terms will be much smaller than any so far considered, but they will certainly change from case to case; however, the changes in the transition and initial states should be equivalent, and therefore the difference of the terms for the two states of any one alkyl group should remain constant when we change the alkyl group; and thus these terms, taken collectively, will contribute, once more, only to the constant term of the entropy of activation, and will disappear from the differences of concern to us.

In three places in this sub-section, we have developed parts of the theory of effects of substitution on the frequency factor of reaction rate, and so it seems useful to collect the conclusions, especially as we shall be able to illustrate most of them, both from our numerical calculations, and from our experimental results. First, as to the ponderal entropy effect, we have concluded that the introduction of a massive substituent anywhere into a reacting aliphatic molecule, as on passing to a higher homologue, should reduce the frequency factor, although a sufficient loading near the reaction centre will weaken this effect and might conceivably reverse it. Secondly, in so far as bulk is associated with the added mass, and if the substituent is sufficiently close to the reaction centre for the bulk to be effective, a steric entropy effect will arise, which may either increase or decrease the frequency factor of reaction rate; and the tendency will be towards an increase if the steric thrust on the attacking reagent is predominantly outwards, but towards a decrease if its main effect is to deflect the reagent sideways. These are further effects that the elementary idea of steric hindrance would not lead one to expect. Thirdly, we have in principle to envisage polar entropic effects of the substituent, which could conceivably change the shape of the transition-state energy surface, and also alter the entropy of some of the solvent molecules around it in a non-self-balancing way. However, such effects

may well prove to be unimportant in saturated aliphatic molecules without strongly polar substituents, and we certainly expect them to be negligible in simple alkyl groups.*

The results of our entropy calculations are given, and compared with the kinetic observations, in Section D.

(C) OBSERVED ARRHENIUS ENERGIES OF ACTIVATION AND THEIR COMPARISON WITH CALCULATED VALUES.

(a) *Observed Arrhenius Energies of Activation of Seven Bimolecular Finkelstein Substitutions with Seven Alkyl Groups.*—Because of our ignorance of the heat-contents of the initial states, and still more of the transition states, of reactions, Arrhenius energies of activation, though they contain heat-content differences, and thereby lack theoretical simplicity, constitute as useful an experimental approach as any we may make to the problem of the structure-dependence of the energies of activation of reacting systems. We therefore begin this comparison of experimental with the calculated results by collecting in Table 5 the Arrhenius energies of activation obtained from the experimental kinetic studies recorded in the seven preceding papers. (Here, as elsewhere, *neoPe* stands for *neopentyl*.)

TABLE 5. *Observed Arrhenius energies of activation (E_A in kcal. mole⁻¹) of bimolecular Finkelstein substitutions in acetone.*

R	Me	Et	Pr [†]	Bu [†]	Pr ^a	Bu [†]	<i>neoPe</i>
(1) Cl ⁻ + RCl	20.2	21.5	—	—	—	—	—
(2) Cl ⁻ + RBr	15.7	17.6	18.6	21.0	17.8	18.3	21.7
(3) Cl ⁻ + RI	16.0	17.2	17.6	—	17.4	17.8	22.0
(4) Br ⁻ + RBr	15.8	17.5	19.7	21.8	17.5	18.9	22.0
(5) Br ⁻ + RI	16.3	17.7	18.5	—	17.9	18.8	23.2
(6) I ⁻ + RBr	16.3	18.9	20.5	22.0 *	19.0	19.9	24.2
(7) I ⁻ + RI	—	17.4	19.4	21.4	—	—	22.2

* Potassium iodide had to be used in the experiments from which this figure is derived. All the other figures in the Table were obtained by the use of lithium salts.

TABLE 6. *Increments due to alkyl homology (ΔE_A in kcal. mole⁻¹) in observed Arrhenius energies of activation of Finkelstein substitutions in acetone.*

R	Me	Et	Pr [†]	Bu [†]	Pr ^a	Bu [†]	<i>neoPe</i>
(1) Cl ⁻ + RCl	0.0	1.3	—	—	—	—	—
(2) Cl ⁻ + RBr	„	1.9	2.9	5.3	2.1	2.6	6.0
(3) Cl ⁻ + RI	„	1.2	1.6	—	1.4	1.8	6.0
(4) Br ⁻ + RBr	„	1.7	3.9	6.0	1.7	3.1	6.2
(5) Br ⁻ + RI	„	1.4	2.2	—	1.6	2.5	6.9
(6) I ⁻ + RBr	„	2.6	4.2	6.9 *	2.7	3.6	7.9
(7) I ⁻ + RI †	„	1.7	3.7	5.7	—	—	6.5

* Since one of the two activation energies, of which this is a difference, had to be obtained by the use of potassium iodide, instead of lithium iodide (cf. note under Table 5), the activation energy subtracted from it, in order to give the figure here entered, is the methyl activation energy obtained comparably, not the value for methyl entered in Table 5.

† The figures in this row are based on an assumed E_A value of 15.7 kcal. mole⁻¹ for the methyl group, a figure estimated by survey of the other methyl-ethyl differences, as well as such general differences as can be seen between the figures of one row and another. Therefore the ethyl figure in this row should be regarded as assumed.

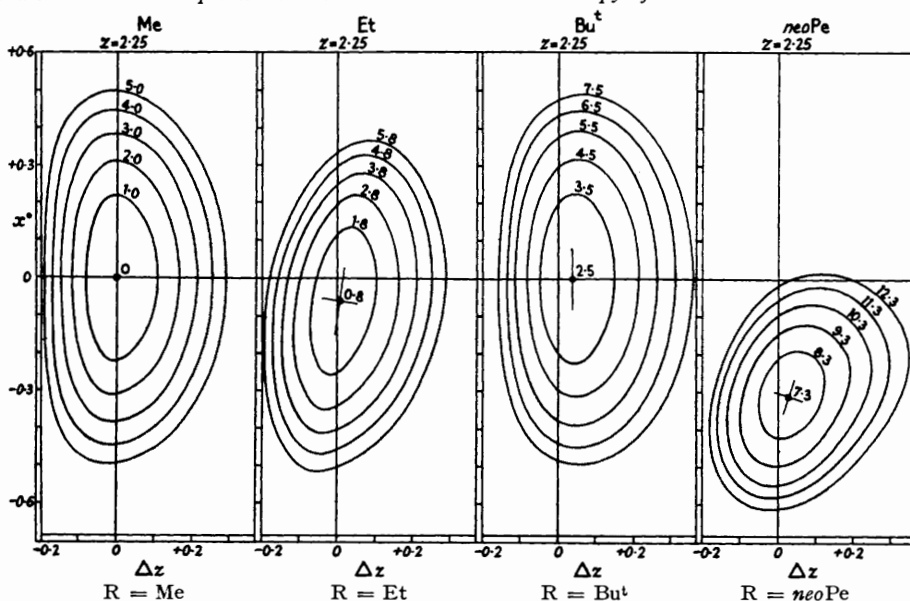
Our object is to consider the kinetic effect on these reactions of those structural changes which convert the methyl group into the higher alkyl groups. If there are either polar or steric effects, we can only define them relatively, and with reference to the methyl group as standard. Therefore, the experimental energy quantities that we shall seek to relate to theory are the excesses, for each Finkelstein substitution, of the Arrhenius energies of activation of the higher alkyl groups over that of the methyl group. These excesses are given, for ready reference, in Table 6.

One of the more general features of Table 6 is that, notwithstanding the scatter of the

* In Ivanoff and Magat's theory, the whole entropic effect of alkyl structure on reaction rate is described as steric (*J. Chim. phys.*, 1950, **47**, 914). This cannot be correct, as is implicit in the formulæ of Bauer and Magat (*ibid.*, p. 922). On the other hand, Ivanoff and Magat's treatment has the merit of being very simple.

figures in any one column, they exhibit no very marked general dependence on the nature of the involved halogens. Dostrovsky, Hughes, and Ingold predicted this theoretically (*loc. cit.*). That polar effects in the alkyl structures should not be much affected by the nature of the halogens is not surprising, because polar effects often conform to linear free-energy relations, and the polarities of halogen atoms are somewhat closely grouped. But that the steric effects, which are believed to be responsible for a large part of the differences of activation energy, should be insensitive to the sizes of the halogens, does at first sight seem surprising; and this conclusion was offered by the authors cited as an example of a prediction that the classical theory of steric hindrance could not have made, but which could be made on the basis of the reconstructed theory.

FIG. 3. Calculated energy surfaces for the reactions $\text{Br}^- + \text{RBr} \rightarrow \text{BrR} + \text{Br}^-$. The figures against the contours are energy co-ordinates in kcal. mole⁻¹, reckoned from the lowest point of the methyl surface as zero. For explanation of the spatial co-ordinates, see Fig. 1. The configurations which by calculation the transition states would have in the absence of steric hindrance are indicated by the intersections (0,0) of the co-ordinates shown, whilst their actual calculated configurations are marked ●. The relative heights of the surfaces control the calculated contribution of steric hindrance to the energy of activation, and their relative shapes its calculated contribution to the entropy of activation.



A second general feature of Table 6 is that, in all reactions, the activation energies rise with homology, but in different ways in the α - and β -methylated series. Along the α -series, Me, Et, Pr^i , Bu^t , the rise can be described as roughly steady, if we make a generous allowance for the irregularities. Along the β -series, Et, Pr^n , Bu^i , neoPe, the rise across the first interval is insignificant, across the second moderate, and across the third large. These are just the trends which Dostrovsky, Hughes, and Ingold deduced by their calculation, though the main experimental support they had at the time consisted of four activation energies, providing only two next-homologue differences, for the alkaline ethanolysis of the alkyl bromides.

There is one further, but less general, feature in Table 6, *viz.*, the tendency to high values in the reaction $\text{I}^- + \text{RBr}$. But the presumed cause of this is such that its discussion is more appropriately given in a paper, at present in draft, which belongs to another series.

Some of the so-called irregularities in Table 6 could probably be discussed in relation to constitution; but we make no such attempt, because of the difficulty of sorting them out unambiguously from the real irregularities, due to disregarded heat-content terms, and to observational error.

(b) *Calculated Configurations of Transition States and Calculated Steric Contributions to Activation Energy for Three Symmetrical Finkelstein Substitutions with Seven Alkyl Groups.*—The method of these calculations is described in Section B: for each type of halogen, and each alkyl group, we have first to construct a surface representing energy as a function of the configuration of the reacting system. Each such surface contains a hollow, the bottom of which represents the transition state. Contour diagrams of some of the calculated energy surfaces are shown in Fig. 3.

We deal in this Section only with the positions of the minima, and first with their spatial co-ordinates. As Fig. 3 illustrates in three examples, all alkyl groups, above methyl, displace the minima, that is, the positions of the halogen atoms in the transition states, outwards from the α -carbon atom by some hundredths of an Å. Furthermore, all these groups, with the one exception of the *tert.*-butyl group, displace the minimum sideways by some 5–10 times as much. The spatial co-ordinates of the minima of all the surfaces calculated are given in Table 7. Here Δ_r represents the outward displacement of the halogen atoms

TABLE 7. *Calculated spatial co-ordinates of the transition states in bimolecular Finkelstein substitutions.*

R	z (Å)	Δz (Å)	x° (Å)	r (Å)	Δr (Å)	θ	
$\text{Cl}^- + \text{RCl} \longrightarrow \text{ClR} + \text{Cl}^-$							
Me	2.05	0.00	± 0.00	2.05	0.00	$\pm 0.0^\circ$	—
Et	2.06	0.01	-0.05	2.06	0.01	-1.4	11°
Pr ⁱ	2.07	0.02	$+0.06$	2.07	0.02	$+1.7$	—
Bu ^t	2.08	0.03	± 0.00	2.08	0.03	± 0.0	—
Pr ⁿ	2.06	0.01	-0.05	2.06	0.01	-1.4	11
Bu ⁱ	2.07	0.02	-0.08	2.07	0.02	-2.2	0
<i>neo</i> Pe	2.07	0.02	-0.27	2.09	0.04	-7.4	21
$\text{Br}^- + \text{RBr} \longrightarrow \text{BrR} + \text{Br}^-$							
Me	2.25	0.00	± 0.00	2.25	0.00	$\pm 0.0^\circ$	—
Et	2.26	0.01	-0.06	2.26	0.01	-1.5	11°
Pr ⁱ	2.27	0.02	$+0.08$	2.27	0.02	$+2.0$	—
Bu ^t	2.29	0.04	± 0.00	2.29	0.04	± 0.0	—
Pr ⁿ	2.26	0.01	-0.06	2.26	0.01	-1.5	11
Bu ⁱ	2.28	0.03	-0.09	2.28	0.03	-2.3	0
<i>neo</i> Pe	2.28	0.03	-0.31	2.30	0.05	-7.7	21
$\text{I}^- + \text{RI} \longrightarrow \text{IR} + \text{I}^-$							
Me	2.46	0.00	± 0.00	2.46	0.00	$\pm 0.0^\circ$	—
Et	2.47	0.01	-0.08	2.47	0.01	-1.9	11°
Pr ⁱ	2.48	0.02	$+0.11$	2.48	0.02	$+2.5$	—
Bu ^t	2.50	0.04	± 0.00	2.50	0.04	± 0.0	—
Pr ⁿ	2.47	0.01	-0.08	2.47	0.01	-1.9	11
Bu ⁱ	2.49	0.03	-0.11	2.49	0.03	-2.5	0
<i>neo</i> Pe	2.50	0.04	-0.39	2.53	0.07	-8.8	22

in the transition state, and x° their lateral displacement; whilst Δ_r is the increase in the length of a halogen semi-bond, 2θ the angle by which the split XRX-bond is bent, and ϕ' is the angle through which the plane of bending is twisted relatively to the stem from C_α of the group responsible for the bending. One sees that by far the largest deformations of the split bond are those produced by the *neopentyl* group, which, in the iodine reaction, lengthens it by 0.14 Å, bends it by 17.6°, and twists the plane of bending away from the stem of the group by 21°. All this has a great effect on the energy at the minimum.

We now turn to the energy co-ordinates. The energy of steric hindrance (or, of steric retardation, since a kinetic, not a thermodynamic, problem is under discussion), due to any group R, is in principle defined as a second difference:

$$W_s(\text{R}) = (W_{\text{R}}^{\text{transition}} - W_{\text{Me}}^{\text{transition}}) - (W_{\text{R}}^{\text{initial}} - W_{\text{Me}}^{\text{initial}})$$

But in calculations by our method, in the cases we have studied, the second term in parentheses, if not zero, is always negligible. Left with the first main term, we set the zero of energy at $W_{\text{Me}}^{\text{transition}}$, and thus introduce the convenient approximate definition,

$$W_s(\text{R}) = W_{\text{R}}^{\text{transition}}$$

That is, the energies of steric retardation of our reactions can with sufficient accuracy be identified with the energy co-ordinates of the minima of the calculated reaction surfaces.

These co-ordinates are in Table 8, in compiling which the opportunity has been taken to illustrate the effects of the successive relaxations that have been allowed to modify the model originally used by Dostrovsky, Hughes, and Ingold. This "stiff" model, yielded an energy curve and did not allow its shape to change: energies thus calculated by them or by ourselves, are headed W_s^{st} in Table 8. In a few cases, the previous authors tried

TABLE 8. *Calculated energies of steric retardation in bimolecular Finkelstein substitutions (kcal. mole⁻¹).*

	Cl ⁻ + RCl → ClR + Cl ⁻			Br ⁻ + RBr → BrR + Br ⁻			I ⁻ + RI → IR + I ⁻		
	W_s^{st}	W_s^{el}	W_s^{pl}	W_s^{st}	W_s^{el}	W_s^{pl}	W_s^{st}	W_s^{el}	W_s^{pl}
Me	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Et	1.1	—	0.8	0.9	—	0.8	0.8	—	0.7
Pr ⁱ	2.2	2.0	1.6	1.9	1.8	1.6	1.4	1.4	1.3
Bu ^t	3.2	2.8	2.8	2.8	2.5	2.5	2.2	2.0	2.0
Pr ⁿ	1.1	—	0.8	0.9	—	0.8	0.8	—	0.7
Bu ⁱ	2.5	—	2.1	2.8	—	2.3	3.2	—	2.5
neoPe	11.5	10.8	6.5	13.9	12.9	7.3	~20	~18	7.8

allowing the semi-bonds to stretch, thereby employing what we might call the "elastic" model, which also gave an energy curve, but allowed its shape to change: the energies which they, or we, have calculated on this basis are headed W_s^{el} . Our "plastic" model allows both stretching and bending, yields an energy surface, and permits its shape to change: these energies are headed W_s^{pl} . We have not yet done any calculations with the other possible model of intermediate type, the "flexible" model, which would allow bending but not stretching; but it would probably be a useful model for getting certain approximate results with the least labour.

Three general features of these theoretical results may be noted. The first is that the relaxation of the restriction on bending, in all cases in which bending could occur, lowers appreciably the calculated steric energies, and greatly lowers the high energies. The most striking of these effects are seen in the reactions of the *neopentyl* group. The early guess that the energetic effect of permitting bending would be of the order of four times that of allowing stretching, and that, accordingly, much of the large discrepancy between the previously calculated steric energy for the bromine-exchange reaction of the *neopentyl* group, and the observed activation energy of the alkaline ethanolsis of *neopentyl* bromide, would disappear if bending were taken into account, is seen to be broadly confirmed.

The reasonableness of expecting to be able thus to compare two such different substitutions as the bromine exchange and alkaline ethanolsis involved another "guess," which was that energies of steric retardation in bimolecular nucleophilic substitution in saturated systems would be found to be only mildly dependent on the sizes of the entering and displaced groups. In Table 8, we see that the steric energies, calculated with the "plastic" model, for the iodine-exchange reaction, never differ very much from those similarly computed for the chlorine-exchange reaction; and, moreover, that the energies of the iodine reaction are not only sometimes greater, but are also sometimes less, than the energies of the chlorine reaction. The reason for the two directions which this difference may take is that the increased outward pressure which acts on the larger halogen adds its potential to others, including that of a Morse curve which has been displaced outwards, and hence provides less energy in the relevant region, whereas the increased lateral pressure adds its potential to others, including that of an undisplaced harmonic curve.

Finally, with regard to the effect of alkyl structure on steric energy, the new calculations confirm the old qualitatively, though not quantitatively. We find the same sharp distinction between the α - and β -methylated series. In the α -series, Me, Et, Prⁱ, Bu^t, the steric energy rises, not regularly in principle as before (for it is an artefact of the "stiff" model that α -substituents act independently), but still, very nearly regularly. On the other hand, along the β -series, Et, Prⁿ, Buⁱ, *neoPe*, the successive energy steps steepen markedly, even

though less sharply than before; for it remains true that the first step is zero, whilst the third is by much the largest of any shown by a pair of neighbouring homologues.

(c) *Comparison of Differences of Experimental Arrhenius Energies of Activation with Calculated Steric Contributions to Energies of Activation.*—For bimolecular reactions of ideal solutes in solution, the Arrhenius energy of activation E_A is related to the heat of activation H^\ddagger by the equation, $E_A = H^\ddagger + RT$, so that, for a standard temperature, we can equate corresponding differences in each quantity, and, in particular, write :

$$\Delta E_A = E_A(\text{R}) - E_A(\text{Me}) = H^\ddagger(\text{R}) - H^\ddagger(\text{Me}) = \Delta H^\ddagger$$

We have been measuring the former difference experimentally, and, of the latter, we have been computing the steric portion,

$$\Delta W_S = W_S(\text{R}) - W_S(\text{Me}) = W_S(\text{R})$$

since the methyl group provides our zero. In general, we must expect that other properties of substituents, chemically more specific than their geometry, properties which we summarise as polar, will also contribute to H^\ddagger , and thus to E_A ; and the structural differential of such contributions may be defined as the polar portion of ΔH and of ΔE_A , as follows :

$$\Delta W_P = W_P(\text{R}) - W_P(\text{Me}) = W_P(\text{R}),$$

the methyl group again providing the zero. This definition leads to the simple summation,

$$\Delta E_A = \Delta W_S + \Delta W_P$$

We do not yet know a feasible method of computing the polar contribution ΔW_P without the use of adjustable constants, and so it is of interest to compare experimental values of ΔE_A with calculated values of ΔW_S , and note what the differences suggest as to the values which ΔW_P may have, and as to how these values vary with structure.

Dostrovsky, Hughes, and Ingold noticed that, except that the *neopentyl* group was out of line, for reasons which they thought they understood, their calculated steric energies fell below the relevant differences of experimental activation energy, by amounts which seemed to increase with α -branching. They ascribed the differences to the polar influence on the reaction of α -methyl groups, assuming that β -methyl groups would have relatively very small polar effects at the reaction centre. The conclusion that such polar effects are involved in bimolecular nucleophilic substitution has since been contested by A. G. Evans (*loc. cit.*; *Nature*, 1946, 157, 438; 158, 586; 1947, 159, 166; *Trans. Faraday Soc.*, 1946, 42, 719; Evans, Evans, and Polanyi, *J.*, 1947, 558; cf., however, Hughes and Ingold, *Trans. Faraday Soc.*, 1947, 43, 798, and Dostrovsky, Hughes, and Ingold, *J.*, 1948, 1283), but, in view of the discussion in Section A of this paper, and the further theoretical and experimental examination of the problem summarised in Sections B and C, it seems to be a difficult conclusion to avoid, even on physicochemical grounds, supposing that one remained unimpressed by the extensive organic-chemical evidence in favour of polar effects on such reactions.*

For simplicity of illustration, we shall make the approximation of assuming that the

* In the first of the papers cited, Evans reported a theoretical study of Finkelstein iodine-exchange for the *tert.*-butyl group with reference to its calculated steric energy, which, he believed, would account for the whole of the experimental excess of the activation energy of this reaction over that of the corresponding reaction of the methyl group. His calculated steric energy, 2 kcal. mole⁻¹, agrees, despite differences of method (cf. Section A), with our calculated value 2.0 kcal. mole⁻¹ (Table 8). Evans's only comment on his value was that the experimental excess of activation energy was (in 1947) unknown. However, there was at that time a clear indication in the work of le Roux, Lu, Sugden, and Thompson (*J.*, 1945, 586) on Finkelstein bromine-exchange for *n*- and *tert.*-butyl in ethylene diacetate, that the excess of energy from methyl to *tert.*-butyl for that reaction would be at least 5 kcal. mole⁻¹. It has now been found to be 6.0 kcal. mole⁻¹ in acetone, the corresponding value for the iodine-exchange being close to 6.5 kcal. mole⁻¹ (cf. Tables 5 and 6). It is therefore not obvious how Evans reached his conclusion that nothing beyond steric hindrance was required to account for differences in energy of activation in the bimolecular reactions of alkyl halides.

polar effects ΔW_P of α -methyl substituents on the activation energies of our reactions may be taken as independent, and that those of the β -substituents may be neglected. Then it is found that the single rounded value 1 kcal. mole⁻¹, for the polar effect ΔW_P of an α -alkyl substituent, brings all the computed totals into approximate agreement with the experimental differences of activation energy ΔE_A , except for one discrepancy of a not unreasonable magnitude just where we might expect it. Two illustrations of this are given in Table 9. First, the comparison is made for an individual Finkelstein substitution: we choose bromine-exchange, because it is one of the reactions for which calculations have been completed, and, on the experimental side, it is one of the most satisfactorily studied. The necessary figures are taken from Tables 6 and 8 (W_S^{pl} values from the latter). Then because the nature of the halogen makes so little systematic difference to either calculated or experimental figures, we average, for each alkyl group, all the available figures in Table 6, and all those (W_S^{pl} values) in Table 8, and make the comparison with the averages. In each illustration, the only notable discrepancy is with the *neopentyl* group, where the calculated compression energies are so large, that the prohibition, by even the "plastic" model, of alkyl deformation will constitute an approximation, the effect which we would expect to notice in our results.

TABLE 9. *Comparison of calculated and observed effects of alkyl structure on energies of activation (kcal. mole⁻¹).*

	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
	<i>Reaction: Br⁻ + RBr \longrightarrow BrR + Br⁻</i>						
ΔW_S	0	0.8	1.6	2.5	0.8	2.3	7.3
ΔW_P	0	1	2	3	1	1	1
ΔE_A (calc.)	0	1.8	3.6	5.5	1.8	3.3	8.3
ΔE_A (obs.)	0	1.7	3.9	6.0	1.7	3.1	6.2
Difference	0	+0.1	-0.3	-0.5	+0.1	+0.2	+2.1
	<i>Averages for all investigated reactions.</i>						
ΔW_S	0	0.8	1.5	2.4	0.8	2.3	7.2
ΔW_P	0	1	2	3	1	1	1
ΔE (calc.)	0	1.8	3.5	5.4	1.8	3.3	8.2
ΔE (obs.)	0	1.7	3.1	6.0	1.9	2.7	6.6
Difference	0	+0.1	+0.4	-0.6	-0.1	+0.6	+1.6

The retarding polar effect, to which our results point, evidently belongs to the class of polar effect on bimolecular substitutions in alkyl compounds, which was identified with the positive inductive effect (+*I*) in some of the earliest papers on nucleophilic substitution (Hughes, Ingold, and Patel, *J.*, 1933, 526; Gleave, Hughes, and Ingold, *J.*, 1935, 236; Hughes and Ingold, *J.*, 1935, 244). This identification assumes that, in simple alkyl halides, the bound halogen atom is so unready to separate as a halide ion that in bimolecular substitution the anionic reagent has to press its attack extensively before a transition state is formed, at which point the two potential anions together will not carry quite the whole of the anionic charge, but will force some of it on to the α -carbon atom. But, as was emphasized in the same period (Hughes, Ingold, and Shapiro, *J.*, 1936, 225), though the point is disregarded in the subsequent arguments of A. G. Evans (*loc. cit.*), the conditions may well be different in bimolecular substitutions of unsaturated halides rendered intrinsically ionisable by an electromeric effect. For then, a considerably less far-pressed attack by an anion may produce a bimolecular transition state in which a total of rather more than a unit of negative charge is claimed by the two would-be anions, leaving a small positive charge on the α -carbon atom, with the result that the positive inductive effect is accelerating.* This overall duality of direction in polar effects in bimolecular substitution, in contrast to their uniformity in unimolecular substitution, has often been noted since.

* Hughes, Ingold, and Shapiro took the benzyl system as their example, as this point was demonstrable from the work of Baker and Nathan (*J.*, 1935, 1844). Catchpole and Hughes later showed that the allyl system behaved similarly (*Trans. Faraday Soc.*, 1941, 37, 207; cf. Vernon, *J.*, 1954, 4462). Without reference to Hughes, Ingold, and Shapiro's discussion of the benzyl case, Evans cites differences between effects of methyl substitution in simple alkyl and in allyl systems as an inconsistency; but it would have been reasonable to assume that the earlier discussion of benzyl would be applicable to allyl.

Other ways of inducing a change of direction of the kinetic polar effect in bimolecular substitution are known, and yet others can be foreseen, but have still to be realised.

(D) OBSERVED ARRHENIUS FREQUENCY FACTORS AND THEIR COMPARISON WITH CALCULATED VALUES.

(a) *Observed Arrhenius Frequency Factors for Seven Bimolecular Finkelstein Substitutions with Seven Alkyl Groups.*—Although the Arrhenius frequency factor B , like the energy of activation E_A , involves heat-capacity terms, it constitutes as good an experimental approach as any available to the problem of the structure-dependence of the entropy changes which accompany activation in reactions. We therefore collect in logarithmic form, in Table 10, the Arrhenius frequency factors, which have been derived from the observations recorded in the seven preceding papers. It should be noted that these values will to some extent be dependent on the salt conditions applying to the measurements. These were approximately standardised along any horizontal row of the Table, but could not be standardised from row to row because different salts are involved. The approximate salt conditions applying to the different rows are as follows: (1) 0.027M-LiCl; (2) 0.07M-LiCl; (3) 0.10M-LiClO₄ + 0.03M-LiCl; (4) 0.024M-LiBr; (5) and (6) 0.024M-LiI; (7) 0.09M-LiI. The negative salt effects of the different salts are probably in the order LiClO₄ > LiI > LiBr > LiCl, and increase, at first markedly, and later more mildly, with increasing salt concentration. If we could bring all the values in the Table to a common salt standard, say that of row (1), the greatest positive correction to log₁₀ B , perhaps 0.5 unit, would be required in row (3), and the other corrections would be smaller in the order

$$(3) > (7) > \underbrace{(5) \text{ and } (6)}_{(2)} > (4) > (1) = \text{zero}$$

Although we have more extensive information on the salt effect than appears in these papers, we still have not enough to make these corrections quantitatively, and so we do not attempt them.

TABLE 10. *Logarithms of observed Arrhenius frequency factors (log₁₀ B , with B in sec.⁻¹ mole⁻¹ l.) of bimolecular Finkelstein substitutions in acetone.*

R	Me	Et	Pr ^l	Bu ^t	Pr ⁿ	Bu ^l	neoPe
(1) Cl ⁻ + RCl	10.3	9.5	—	—	—	—	—
(2) Cl ⁻ + RBr	9.3	8.9	7.9	8.9	8.6	8.4	7.4
(3) Cl ⁻ + RI	9.4	9.1	8.3	—	8.8	8.3	7.9
(4) Br ⁻ + RBr	10.7	10.1	9.7	10.7	9.8	9.6	8.6
(5) Br ⁻ + RI	11.4	11.1	10.2	—	10.8	10.3	10.1
(6) I ⁻ + RBr	11.4	11.0	10.2	10.2 *	10.8	10.3	10.2
(7) I ⁻ + RI	—	11.5	11.0	12.0	—	—	10.2

* See note under Table 5.

Though there are some exceptions, one cannot but notice the general trend towards higher frequency factors, for any one alkyl group, as the atomic number of either halogen is increased, and the near-constancy of the values as between the two reactions, (5) and (6), which use the same pair of halogens with reversed functions. We are not able to offer any very useful discussion of this, because the comparisons involve, not merely the effect of structural changes on the behaviour of a given set of reacting atoms, but also changes in the reacting atoms; with the consequence that the unevaluated terms in our calculated energies and entropies of activation, such as, for example, the solvation entropy of the charged species, are not self-balancing.

When we pass from the frequency factors themselves to the ratios in which they are changed by modifications of the alkyl group, then the problem of interpretation falls much more nearly within our capacity. As our object is to study the kinetic effects of those structural changes which convert the methyl group into higher alkyl groups, we assemble in Table 11 the excesses of the logarithms of the frequency factors for the higher alkyl groups over those for the methyl group.

In these figures we find no general trend, when, for any one alkyl group, the halogens

are changed. Instead, we see irregularities so unsystematic as to make one feel that an average is worth almost as much attention as any individual value.

On the other hand, the differences from one alkyl group to another show consistent common features. Along the α -series, Me, Et, Prⁱ, Bu^t, the differences at first fall, in two considerable steps as far as Prⁱ; and then for Bu^t the values show a sharp rise. This is in

TABLE 11. *Observed increments, due to alkyl homology, in the logarithms of the Arrhenius frequency factors ($\Delta \log_{10} B$, with B in $\text{sec.}^{-1} \text{mole}^{-1} \text{l.}$) of Finkelstein substitutions in acetone.*

R:	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ^l	neoPe
(1) Cl ⁻ + RCl	0.0	-0.8	—	—	—	—	—
(2) Cl ⁻ + RBr	"	-0.4	-1.4	-0.4	-0.7	-0.9	-1.9
(3) Cl ⁻ + RI	"	-0.3	-1.1	—	-0.6	-1.1	-1.5
(4) Br ⁻ + RBr	"	-0.6	-1.0	± 0.0	-0.9	-1.1	-2.1
(5) Br ⁻ + RI	"	-0.3	-1.2	—	-0.6	-1.1	-1.3
(6) I ⁻ + RBr	"	-0.4	-1.2	-0.3 *	-0.6	-1.1	-1.2
(7) I ⁻ + RI †	"	-0.5	-1.0	± 0.0	—	—	-1.8

* See notes under Tables 5 and 6; the figure here entered is the difference of values obtained for the *tert.*-butyl and the methyl group in comparable experimental conditions, with potassium iodide as reagent.

† The figures in this row are based on an assumed $\log_{10} B$ value of 12.0 for the methyl group, a figure estimated by survey of the other methyl-ethyl differences. Therefore the ethyl value in this row is to be regarded as assumed.

marked contrast to the energy variation, which we saw to be almost linear throughout the α -series. In the β -series, Et, Prⁿ, Bu^l, neoPe, the logarithmic differences of frequency fall in substantial steps throughout. The contrast here with the energy variation is that the steps do not progressively steepen throughout the series in the same marked way.

(b) *Calculated Effects of Alkyl Structure on the Entropies of Activation of the Finkelstein Substitution of Bromine Exchange.*—Our programme is to make such calculations for all the Finkelstein substitutions for which we have the energy surfaces; but, whereas our calculations on the bromine exchange reaction are complete, those on other substitutions are not, and are proceeding somewhat slowly. Therefore we have decided to report what is finished, rather than to delay further the publication of our work of the last 9 years.

The method of calculation is described in Section C. In summary, we compute translational, rotational, and vibrational entropies for the initial alkyl halide, and for the transition state. We do not trouble about those entropy terms which are self-balancing in the differences of activation entropy, *viz.*, the translational entropy of the halide ion, and the solvation entropies. Each vibrational entropy is the sum of terms corresponding to the normal vibrations; however, our model, which assumes pliability around the reaction centre, but stiffness in the remainder of the alkyl group, allows us to neglect intra-alkyl vibrations, but requires us to calculate the other vibrational terms with what their frequencies would be if the alkyl groups were stiff. For transition states, the rotational entropies depend on the spatial co-ordinates of the minima of the energy surfaces of the reactions, whilst the vibrational entropies depend on the curvatures of the surfaces around the minima. For the normal states of the *n*-propyl and *isobutyl* groups, we calculate for all conformations, weighting the results equally in the final averages. The detailed results for the calculated parts of the entropies of the transition and initial states are given in Table 12. The notation is explained in Section C, but Figs. 1 and 2 will be a sufficient reminder. A brace indicates vibrations of the same symmetry species, whose entropy contributions, if different, are indeterminately interchangeable.

The effects of structure on the components of the entropy of activation are to be calculated as second differences from the data of Table 12. It is instructive to proceed towards the second differences in both the possible ways, in order to be able to follow structural changes on the entropy of each state, as well as in the activation entropy:

$$S_{\text{R}}^{\ddagger} = S_{\text{R}}^{\text{transition}} - S_{\text{R}}^{\text{initial}}$$

$$\Delta S^{\text{transition}} = S_{\text{R}}^{\text{transition}} - S_{\text{Me}}^{\text{transition}}; \quad \Delta S^{\text{initial}} = S_{\text{R}}^{\text{initial}} - S_{\text{Me}}^{\text{initial}}$$

$$\Delta S^{\ddagger} = S_{\text{R}}^{\ddagger} - S_{\text{Me}}^{\ddagger} = \Delta S^{\text{transition}} - \Delta S^{\text{initial}}$$

The two sets of first differences, and the second differences, are given, in partly summarised form, in Table 13.

The translational entropy of the bromide ion is 13.58 cal. deg.⁻¹ mole⁻¹. This should be added to all initial-state entropies, and subtracted from all entropies of activation. It disappears from the second differences. The solvation entropies are unevaluated, and they too should disappear from the second differences.

These figures illustrate a number of the rules, which in Section B were derived from theory, concerning both ponderal and steric effects of homology on entropy of activation, and thus on the frequency factor of reaction rate. The first is that the ponderal effect of mass apart from its position on the translational entropy produces a decrease in the translational entropy of activation as the molecular weight increases, as is illustrated by the following figures (cal. deg.⁻¹ mole⁻¹):

Me, 1.82; Et, 1.64; Prⁿ and Prⁱ, 1.49; Buⁱ and Bu^t, 1.36; *neo*Pe, 1.26.

The second effect, essentially ponderal, though it involves both mass and position, is that rotational entropy of activation decreases as new masses are added, and does so the

TABLE 12. *Calculated translational, rotational, and vibrational entropies (in cal. deg.⁻¹ mole⁻¹), and their totals, for transition states and initial molecules in the bimolecular substitution, Br⁻ + RBr → BrR + Br⁻.*

		Transition state.		Initial state.	
R = Methyl					
S_t	$(\frac{3}{2})R \ln M$	15.39		$(\frac{3}{2})R \ln M$	13.57
"	Constants	0.52		Constants	0.52
	Total		15.91	Total	14.09
S_r	$(\frac{1}{2})R \ln ABC$	14.60		$(\frac{1}{2})R \ln ABC$	8.98
"	$-R \ln \sigma$	-3.56		$-R \ln \sigma$	-2.18
"	Constants	-3.69		Constants	-3.69
	Total		7.35	Total	3.11
S_v	z_s	3.12		z_1	0.43
"	$\{x_s$	2.24		$\{x_1$	0.11
"	y_s	2.24		y_1	0.11
"	x_a	0.06		Total	0.65
"	y_a	0.06			
	Total		7.72		
S			30.98		17.85
R = Ethyl					
S_t	$(\frac{3}{2})R \ln M$	15.62		$(\frac{3}{2})R \ln M$	13.98
"	Constants	0.52		Constants	0.52
	Total		16.14	Total	14.50
S_r	$(\frac{1}{2})R \ln ABC$	17.10		$(\frac{1}{2})R \ln ABC$	12.55
"	$-R \ln \sigma$	-1.38		$-R \ln \sigma$	0.00
"	Constants	-3.69		Constants	-3.69
	Total		12.03	Total	8.86
S_v	z_s	2.85		z_1	0.76
"	$\{x_s$	2.44		x_1	1.48
"	y_s	2.19		y_1	0.59
"	x_a	1.50		Total	2.83
"	y_a	0.06			
	Total		9.04		
S			37.21		26.19

TABLE 12. (Continued.)

Transition state.			Initial state.		
R = isoPropyl					
S_i	$(\frac{2}{3})R \ln M$	15.83		$(\frac{2}{3})R \ln M$	14.34
"	Constants	0.52		Constants	0.52
	Total		16.35	Total	
S_r	$(\frac{1}{2})R \ln ABC$	17.85		$(\frac{1}{2})R \ln ABC$	14.58
"	$-R \ln \sigma$	-1.38		$-R \ln \sigma$	0.00
"	Constants	-3.69		Constants	-3.69
	Total		12.78	Total	
S_o	z_o^*	2.65		z_1	0.94
"	x_o^*	2.65		x_1	1.04
"	y_o	2.13		y_1	2.13
	Total			Total	
"	x_o	0.92			4.11
"	y_o	1.69			
	Total		10.04		
S			39.17		29.86
R = tert.-Butyl					
S_i	$(\frac{2}{3})R \ln M$	16.03		$(\frac{2}{3})R \ln M$	14.67
"	Constants	0.52		Constants	0.52
	Total		16.55	Total	
S_r	$(\frac{1}{2})R \ln ABC$	18.30		$(\frac{1}{2})R \ln ABC$	15.60
"	$-R \ln \sigma$	-3.56		$-R \ln \sigma$	-2.18
"	Constants	-3.69		Constants	-3.69
	Total		11.05	Total	
S_o	z_o	3.46		z_1	1.09
"	x_o	3.41		x_1	2.14
"	y_o	3.41		y_1	2.14
	Total			Total	
"	x_o	2.21			5.37
"	y_o	2.21			
	Total		14.70		
S			42.30		30.29
R = n-Propyl					
S_i	$(\frac{2}{3})R \ln M$	15.83		$(\frac{2}{3})R \ln M$	14.34
"	Constants	0.52		Constants	0.52
	Total		16.35	Total	
S_r	$(\frac{1}{2})R \ln ABC$	18.30		$(\frac{1}{2})R \ln ABC$:	14.86
"	$-R \ln \sigma$	-1.38		anti	14.34
"	Constants	-3.69		each syn	14.63
	Total		13.27	Average	
"				$-R \ln \sigma$	14.53
"				Constants	0.00
"				Constants	-3.69
	Total			Total	
S_o	z_o	3.01		z_1	0.96
"	x_o	2.58		x_1 : anti	2.32
"	y_o	2.19		each syn	2.11
	Total			Average	
"	x_o	2.15		y_1 : anti	2.18
"	y_o	0.06		each syn	0.79
	Total		9.99	Average	
"				Total	0.95
"				Total	4.09
S			39.61		29.79

TABLE 12. (Continued.)

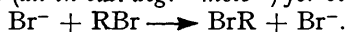
Transition state.			R = isoButyl		Initial state.	
S_t	$(\frac{3}{2})R \ln M$	16.03		$(\frac{3}{2})R \ln M$	14.67	
"	Constants	0.52		Constants	0.52	
"	Total		16.55	Total		15.19
S_r	$(\frac{1}{2})R \ln ABC$	18.85		$(\frac{1}{2})R \ln ABC$:		
"	$-R \ln \sigma$	-1.38		<i>anti</i>	15.70	
"	Constants	-3.69		each <i>syn</i>	15.85	
"	Total		13.78	Average	15.80	
"				$-R \ln \sigma$	0.00	
"				Constants	-3.69	
S_o				Total		12.11
"	z_1	3.06		z_1	1.09	
"	x_1	2.54		x_1 : <i>anti</i>	2.28	
"	y_1	2.19		each <i>syn</i>	2.54	
"	x_a	2.35		Average	2.45	
"	y_a	0.06		y_1 : <i>anti</i>	1.05	
"	Total		10.20	each <i>syn</i>	1.40	
"				Average	1.28	
"				Total		4.82
S			40.53			32.12
R = neoPentyl						
S_t	$(\frac{3}{2})R \ln M$	16.22		$(\frac{3}{2})R \ln M$	14.96	
"	Constants	0.52		Constants	0.52	
"	Total		16.74	Total		15.48
S_r	$(\frac{1}{2})R \ln ABC$	19.37		$(\frac{1}{2})R \ln ABC$	16.68	
"	$-R \ln \sigma$	-1.38		$-R \ln \sigma$	0.00	
"	Constants	-3.69		Constants	-3.69	
"	Total		14.30	Total		12.99
S_o	z_1	2.84		z_1	1.18	
"	x_1	2.62		x_1	2.70	
"	y_1	2.19		y_1	1.50	
"	x_a	1.98		Total		5.38
"	y_a	0.06				
"	Total		9.69			
S			40.73			33.85

Note: The frequencies of the two vibrations marked with an asterisk are not identical in principle, but, as calculated, they were complex, differing only by an imaginary part, which was neglected. Their values were $(10^{13}/2\pi) (8.29 \pm 0.52i)^{\frac{1}{2}}$ sec.⁻¹. They were the only calculated frequencies to emerge in complex form.

more markedly the nearer the added masses are to the reaction centre. The following figures illustrate these effects of homology and of position-isomerism (cal. deg.⁻¹ mole⁻¹):

Me, 4.24; Et, 3.17; Prⁿ, 2.62; Prⁱ, 2.47; Buⁱ, 1.67; Bu^t, 1.32; neoPe, 1.31.

The comparison of Bu^t with neoPe shows that the effect of shifting two methyl groups from the α - to the β -position almost cancels that of adding a third methyl group. Conformational isomerism does not follow such simple rules, for the reason that when we transfer two main masses, relatively to two between them, from *anti*- to *syn*-positions, the displacement brings them closer longitudinally, but also has a transverse component which moves them further off what was before the main line or plane of masses. We can see this conflict

TABLE 13. *Calculated effects of alkyl structure on entropies of transition and initial states, and on activation entropies (all in cal. deg.⁻¹ mole⁻¹) for bimolecular reactions:*

	$S_{\text{R}}^{\text{transition}}$	$S_{\text{R}}^{\text{initial}}$	S_{R}^{\ddagger}	Differences from methyl		
				$\Delta S^{\text{transition}}$	$\Delta S^{\text{initial}}$	ΔS^{\ddagger}
			<i>Methyl</i>			
Transl.	15.91	14.09	1.82	0.00	0.00	0.00
Rotn.	7.35	3.11	4.24	"	"	"
Vibrn.	7.72	0.65	7.07	"	"	"
Total	30.98	17.85	13.13	"	"	"
			<i>Ethyl</i>			
Transl.	16.14	14.50	1.64	0.23	0.41	-0.18
Rotn.	12.03	8.86	3.17	4.68	5.75	-1.07
Vibrn.	9.04	2.83	6.21	1.32	2.18	-0.86
Total	37.21	26.19	11.02	6.23	8.34	-2.11
			<i>isoPropyl</i>			
Transl.	16.35	14.86	1.49	0.44	0.77	-0.33
Rotn.	12.78	10.89	1.89	5.43	7.78	-2.35
Vibrn.	10.04	4.11	5.93	2.32	3.46	-1.14
Total	39.17	29.86	9.31	8.19	12.01	-3.82
			<i>tert.-Butyl</i>			
Transl.	16.55	15.19	1.36	0.64	1.10	-0.46
Rotn.	11.05	9.73	1.32	3.70	6.62	-2.92
Vibrn.	14.70	5.37	9.33	6.98	4.72	+2.26
Total	42.30	30.29	12.01	11.32	12.44	-1.12
			<i>n-Propyl (anti-conformation)</i>			
Transl.	16.35	14.86	1.49	0.44	0.77	-0.33
Rotn.	13.27	10.65	2.62	5.92	7.54	-1.62
Vibrn.	9.99	4.56	5.43	2.27	3.91	-1.64
Total	39.61	30.07	9.54	8.63	12.22	-3.59
			<i>n-Propyl (D- or L-syn-conformation)</i>			
Transl.	16.35	14.86	1.49	0.44	0.77	-0.33
Rotn.	13.27	10.94	2.33	5.92	7.83	-1.91
Vibrn.	9.99	3.86	6.13	2.27	3.21	-0.94
Total	39.61	29.66	9.95	8.63	11.81	-3.18
			<i>n-Propyl (average)</i>			
Transl.	16.35	14.86	1.49	0.44	0.77	-0.33
Rotn.	13.27	10.84	2.43	5.92	7.73	-1.81
Vibrn.	9.99	4.09	5.90	2.27	3.44	-1.17
Total	39.61	29.79	9.82	8.63	11.74	-3.31
			<i>isoButyl (anti-conformation)</i>			
Transl.	16.55	15.19	1.36	0.64	1.10	-0.46
Rotn.	13.78	12.01	1.77	6.43	8.90	-2.47
Vibrn.	10.20	4.42	5.78	2.48	3.77	-1.29
Total	40.53	31.62	8.91	9.55	13.77	-4.22
			<i>isoButyl (D- or L-syn-conformation)</i>			
Transl.	16.55	15.19	1.36	0.64	1.10	-0.46
Rotn.	13.78	12.16	1.62	6.43	9.05	-2.62
Vibrn.	10.20	5.03	5.17	2.48	4.38	-1.90
Total	40.53	32.38	8.15	9.55	14.53	-4.98
			<i>isoButyl (average)</i>			
Transl.	16.55	15.19	1.36	0.64	1.10	-0.46
Rotn.	13.78	12.11	1.67	6.43	9.00	-2.57
Vibrn.	10.20	4.82	5.38	2.48	4.17	-1.69
Total	40.53	32.12	8.41	9.55	14.27	-4.72
			<i>neoPentyl</i>			
Transl.	16.74	15.48	1.26	0.83	1.39	-0.56
Rotn.	14.30	12.99	1.31	6.95	9.88	-2.93
Vibrn.	9.69	5.38	4.31	1.97	4.73	-2.76
Total	40.73	33.85	6.88	9.75	16.00	-6.25

of influences in the following figures (cal. deg.⁻¹ mole⁻¹), noting that a methyl and halogen which are *anti*-related in *syn*-Bu^l, become *syn*-related in the *anti*-isomer:

anti-Prⁿ, 2.62; *syn*-Prⁿ, 2.33. *syn*-Bu^l, 1.62; *anti*-Bu^l, 1.77.

The third ponderal effect is on vibrational entropy, and will cause the vibrational entropy of activation to decrease as new masses are added, except possibly when sufficient are introduced near the reaction centre. Added to this, there are steric effects in either direction on vibrational entropy, inasmuch as outward pressure on the reagent will increase the vibrational entropy of activation, whilst lateral pressure will decrease it. Our figures, given below (cal. deg.⁻¹ mole⁻¹), do not enable these effects to be clearly sorted out in every case: but they do show the ponderal retarding factor substantially in isolation in the difference from ethyl to *n*-propyl, the steric effects of which are identical; and they show the importance of the accelerating factors strikingly in the figure for *tert*.-butyl:

Me, 7.07; Et, 6.21; Prⁿ, 5.90; Prⁱ, 5.93; Bu^l, 5.38; Bu^t, 9.33; *neo*Pe, 4.31.

Conformational isomerism involves conflicting effects on vibrational entropy, for reasons analogous to those discussed above; but it happens that in both the examples for which we have calculated it, the vibrational entropy of activation increases with those conformational changes which predominantly bring remote masses closer, as the following figures show (cal. deg.⁻¹ mole⁻¹):

anti-Prⁿ, 5.43; *syn*-Prⁿ, 6.13. *syn*-Bu^l, 5.17; *anti*-Bu^l, 5.78.

It is of interest completely to separate the ponderal and the steric effect on entropy in order to see more clearly how each depends on structure. For the transition states, we can do this by recalculating their entropy with the supposition that all have the same energy surface as the methyl transition state, an assumption which excludes effects of steric hindrance. The translational entropies then remain unchanged; for they are in any case modified by structure only through the ponderal effect. The rotational entropies are changed slightly; for, in the absence of the imposed restriction, their structural modification is mainly ponderal, though it contains a very small steric element. On the other hand, the vibrational entropies, which, in the natural case, are modified by both the ponderal and the steric effect to an important degree, are considerably changed when the steric effect is thus artificially removed. The transition-state entropies, as they would be under the ponderal effect as the only structural influence, are shown in Table 14.

TABLE 14. *Calculated entropies (in cal. deg.⁻¹ mole⁻¹) for transition states of the bimolecular substitution, Br⁻ + RBr → BrR + Br⁻, with the ponderal effect as the only structural influence, steric effects being excluded.*

R:	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ^l	<i>neo</i> Pe
	<i>Details of the vibrational entropy.</i>						
Vib. z_s	3.12	3.12	3.12	3.12	3.12	3.12	3.12
„ x_s	2.24	2.79	3.09	3.31	3.09	3.31	3.45
„ y_s	2.24	2.19	2.13	3.31	2.19	2.19	2.19
„ x_a	0.06	1.61	1.21	2.10	2.39	2.67	3.01
„ y_a	0.06	0.06	2.06	2.10	0.06	0.06	0.06
	<i>Parts of the total entropy</i>						
Translation	15.91	16.14	16.35	16.55	16.35	16.55	16.74
Rotation	7.35	11.96	12.83	10.98	13.17	13.69	14.02
Vibration	7.72	9.77	11.61	13.94	10.76	11.35	11.83
	<i>Total entropy</i>						
	30.98	37.87	40.79	41.47	40.28	41.59	42.59

We can now isolate the ponderal effect on the entropies of the transition states by subtracting the entropy terms for the methyl group from corresponding terms for the higher alkyl groups. This is done in the uppermost part of Table 15. By subtracting

these figures from corresponding figures for the combined ponderal and steric effects on the entropy of transition states, as given in Table 13 (column 5), we isolate the steric effect on the entropies of the transition states. These values are in the central part of Table 15; and, at the foot of the Table, a summary is given of the ponderal and the steric contributions.

TABLE 15. *Calculated ponderal and steric effects (in cal. deg.⁻¹ mole⁻¹) on the entropy of transition states of the bimolecular substitutions, Br⁻ + RBr → BrR + Br⁻.*

R:	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
<i>Details of the ponderal contribution</i>							
Translation	0.00	0.23	0.44	0.64	0.44	0.64	0.83
Rotation	„	4.61	5.38	3.63	5.82	6.34	6.67
Vibration	„	2.05	3.89	6.22	3.04	3.63	4.11
<i>Details of the steric contribution</i>							
Rotation	0.00	0.07	0.05	0.07	0.10	0.09	0.28
Vibration	„	-0.73	-1.57	0.76	-0.77	-1.15	-2.14
<i>Summary of the contributions</i>							
Ponderal	0.00	6.89	9.71	10.49	9.30	10.61	11.61
Steric	„	-0.66	-1.52	0.83	-0.67	-1.06	-1.86
Total	0.00	6.23	8.19	11.32	8.63	9.55	9.75

We see that the ponderal effect is positive, and increases with molecular weight. Amongst isomers, it shows only small changes of no consistent trend. This is because, although in accordance with the considerations indicated earlier, the rotational part becomes less positive with increased α -branching, the vibrational part shows opposing differences, largely for the reason that in some of the vibrations, y_a particularly, we do not, as already explained, regard the whole alkyl group as coupled in its motion with that of the halogens. We see that the steric effect varies as we should expect from qualitative inspection of the energy surfaces, being positive for the *tert.*-butyl group, and negative for all other groups.

Turning to the initial states, the situation is simple in that our calculations do not show that they suffer appreciable steric deformation. Therefore the entropies of initial states, as entered in Table 13 (column 3), are structurally modified through the ponderal effect only; and the structural modifications, as given in Table 13 (column 5), accurately represent the ponderal modifications.

By subtracting the initial-state entropies of Table 13 (column 3) from the transition-state entropies of Table 14, we obtain entropies of activation as they would be in the absence of a steric effect. The values are in Table 16. It should be noted that, although in most stable molecules vibrational entropies are considerably smaller than either translational or rotational entropies, this is not altogether true for transition states, because of the ease of deformation of the semi-bonds, and therefore it is not true for entropies of activation.

TABLE 16. *Calculated entropies of activation (in cal. deg.⁻¹ mole⁻¹) for the bimolecular substitution, Br⁻ + RBr → BrR + R⁻, with the assumption that the ponderal effect is the only structural effect.*

R:	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
Translation	1.82	1.64	1.49	1.36	1.49	1.36	1.26
Rotation	4.24	3.10	1.84	1.25	2.33	1.58	1.03
Vibration	7.07	6.94	7.50	8.57	6.67	6.53	6.45
Total	13.13	11.68	10.83	11.18	10.49	9.47	8.74

If we subtract the methyl entropy terms of Table 16 from corresponding terms for the higher alkyl groups, we isolate the ponderal effect on entropy of activation. These values are in the top section of Table 17. By subtracting them from the corresponding values

for the combined ponderal and steric effect on entropy of activation, as given in Table 13 (last column), we isolate the steric effect on this quantity. These figures are in the central part of Table 17. The summary of this analysis is at the foot of the Table. It shows that the ponderal effect on the frequency factor of reaction rate is always retarding. The steric effect is accelerating for the *tert.*-butyl group, but is otherwise retarding, becoming more so as we ascend either the α - or β -methylated homologous series.

TABLE 17. *Calculated components of the structural effect on the entropy of activation (in cal. deg.⁻¹ mole⁻¹) of the bimolecular substitution Br⁻ + RBr → BrR + Br⁻.*

R:	Me	Et	Pr ^t	Bu ^t	Pr ⁿ	Bu ^l	neoPe
		<i>Details of the ponderal effect</i>					
Translation	0.00	-0.18	-0.33	-0.46	-0.33	-0.46	-0.56
Rotation	„	-1.14	-2.40	-2.99	-1.91	-2.66	-3.21
Vibration	„	-0.13	0.43	1.50	-0.40	-0.54	-0.62
		<i>Details of the steric effect</i>					
Rotation	0.00	0.07	0.05	0.07	0.10	0.09	0.23
Vibration	„	-0.73	-1.57	0.76	-0.77	-1.15	-2.1
		<i>Summary of the contributions</i>					
Ponderal	0.00	-1.45	-2.30	-1.95	-2.64	-3.66	-4.39
Steric	„	-0.66	-1.52	+0.83	-0.67	-1.06	-1.86
	0.00	-2.11	-3.82	-1.12	-3.31	-4.72	-6.25

(c) *Comparison of Effects of Alkyl Structure on Experimental Arrhenius Frequency Factors with Calculated Structural Effects on Entropies of Activation.*—With the usual convention of taking separate account of the entropy of motion in the reaction co-ordinate, so that this term can be omitted from the reckoning of transition-state entropies, the relation between the Arrhenius frequency factor B and the entropy of activation S^\ddagger for a bimolecular reaction between ideal solutes is

$$\ln B = S^\ddagger/R + \ln (kT/h) + 1$$

(Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 199).

With the aid of this formula, and of our calculations of the entropy of activation of the parent reaction of bromine-exchange



together with the experimental measurement of its Arrhenius frequency factor, we can estimate the theoretically unevaluated contribution of solvation to the entropy of activation of bromine-exchange in acetone. From the calculated part of the entropy of activation which is entered in Table 13, and the calculated translational entropy of the bromide ion, we find $S_G^\ddagger = -0.45$ cal. deg.⁻¹ mole⁻¹ as the entropy of activation of the reaction in the gaseous state. Introduction of this into the above equation shows that, at the standard temperature, the Arrhenius frequency factor of the gaseous reaction should be given by $\log_{10} B = 13.13$. The observed frequency factor for the reaction in acetone is expressed by $\log_{10} B = 10.7$. Insertion of this into the equation leads to an entropy of activation $S^\ddagger = -11.6$ cal. deg.⁻¹ mole⁻¹. The difference between this and the gaseous value is $S_s = -11.15$ cal. deg.⁻¹ mole⁻¹; and this represents the contribution of solvation, including any salt effect, to the entropy of activation of the reaction in acetone.

Our main object, however, is to compare calculated and observed effects of alkyl structure on the frequency factors of the substitutions; and, for this purpose, we need the above equation only in difference form,

$$\Delta \ln B = \Delta S^\ddagger/R, \text{ or } \Delta \log_{10} B = \Delta S^\ddagger/4.575$$

with ΔS^\ddagger in cal. deg.⁻¹ mole⁻¹, the temperature being standard.

With the observed and calculated values taken from Tables 11 and 13, respectively,

this comparison works out as shown in Table 18. There it is made in two ways, first, with the calculated figures for the bromine-exchange reaction, which is the only Finkelstein substitution for which they are as yet wholly available, and the observed values for the same reaction; and then, in view of the already noticed absence of any trend in the observed values, when, for any alkyl group, the halogens are changed, we compare the calculated figures for bromine-exchange with the averages, for common alkyl groups, of all the measured values.

TABLE 18. *Comparison of observed and calculated effects of alkyl structure on the logarithms of the Arrhenius frequency factors ($\Delta\log_{10} B$).*

	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
Obsd. (Br-exchange reaction)...	0.0	-0.6	-1.0	±0.0	-0.9	-1.1	-2.1
Calc. " " " " " " " " "	0.0	-0.46	-0.84	-0.24	-0.72	-1.03	-1.37
Obsd. (all reactions : means)...	0.0	-0.5	-1.1	-0.2	-0.7	-1.1	-1.6

It will be seen that the calculated frequency factors put all the alkyl groups in the right order, with *tert.*-butyl most like methyl,* *neopentyl* most unlike, and *isopropyl* and *isobutyl* similar to each other, with respect to effects on the frequency factor. Further, in most cases the calculations account nearly quantitatively for the observed values.† The main exceptions are the *tert.*-butyl group, for which the calculated frequency factor seems to be slightly too negative, and the *neopentyl* group for which it is considerably too positive. We think that these discrepancies are due to theoretical over-simplification, most probably to the assumption of stiff alkyl groups. If there is indeed any appreciable compression energy in the initial states of the alkyl halides, despite the fact that calculations by our method find scarcely any, then the *tert.*-butyl group has more entropy of activation to gain than has any other group from the circumstance that, in the transition state, its component parts open like flower petals, so that any previously self-imposed restrictions in the group on its internal movement are relaxed, and the transition state is thus afforded some unreckoned additional entropy. Such an effect of any initial-state compression, if appreciable at all, must be small, even for *tert.*-butyl: it will be considerably smaller, and hence probably unnoticeable, for *isopropyl*; and it will be vanishing in every other case. On the other hand, the *neopentyl* group indubitably has entropy of activation to lose, and much more to lose than has any other group, from the circumstance that its main parts are not only not spread out in the transition state, but must be considerably squeezed together by the outstandingly strong pressures there developed, with the result that new restrictions will be placed on the internal movements of the group, and the transition state will accordingly suffer an unreckoned loss of entropy. This undoubtedly real effect will be much smaller in all other groups, the calculated compression energies of which are all quite small in comparison with those of the *neopentyl* group; and therefore the effect might well pass unnoticed in our results in all cases except that of the *neopentyl* group. With these explanations we feel that Table 18 largely vindicates the method of our calculations, apart from the one assumption of stiff alkyl groups, which is regretfully made only for the abbreviation of arithmetic.

(E) OBSERVED EFFECTS OF ALKYL STRUCTURE ON REACTION RATE AND THEIR COMPARISON WITH CALCULATED VALUES.

(a) *Observed Rates of Seven Bimolecular Finkelstein Substitutions with Seven Alkyl Groups.*—The rates in acetone at 25° of the various substitutions, our experimental study of which is reported in the seven preceding papers, are collected in Table 19. As many of these rates are obtained by interpolation, and some by extrapolation, from observations made at other temperatures, no more than two-figure accuracy is intended by the entries.

We note that, if one halogen is kept fixed while the other is changed, then, no matter

* The peculiar position of the *tert.*-butyl group with respect to frequency factor in bimolecular substitutions was first noticed by Le Roux, Lu, Sugden, and Thompson (*J.*, 1945, 586), who described it as indicating an effective collision area too large to be understood on the basis of the theories of the time.

† The observational error in $\log_{10} B$ is about 0.1.

whether the variable halogen is that of the alkyl halide or that of the halide ion (and, indeed, it would be hard to say from these figures to which type of halogen variation the reaction rate is generally more sensitive), rate always increases from Cl to Br, and nearly always,* though by a much smaller factor, from Br to I. Our previous analysis of these rate changes in terms of variations of the Arrhenius energies of activation and the frequency factors showed that, whilst the rate changes of something over 10^2 from RCl to RBr,

TABLE 19. *Experimentally found second-order rate constants ($10^5 k_2$, with k_2 in sec.^{-1} mole $^{-1}$ l.) for Finkelstein substitutions in acetone at 25°.*

R	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
(1) Cl ⁻ + RCl	3.9	0.050	—	—	—	—	—
(2) Cl ⁻ + RBr	600	9.9	0.13	0.029	6.4	1.5	0.00026
(3) Cl ⁻ + RI	470	42	1.3	—	25	1.6	0.00058
(4) Br ⁻ + RBr	13,000	170	1.8	0.51	110	5.7	0.0026
(5) Br ⁻ + RI	27,000	1490	37	—	1050	32	—
(6) I ⁻ + RBr	25,000	170	1.3	0.10	140	6.0	0.0020
(7) I ⁻ + RI	—	6000	53	18	—	—	0.11

illustrated by the first two rows in the Table, are due mainly to changes in the energy of activation, the remaining rate variations, covering a factor of something under 10^3 , from the second row to the bottom of the Table, are attributable mainly to changes in the frequency factor. It would appear, therefore, that the rate variations down the columns of Table 19 are due, except where bound chlorine is involved, less to any energetic differences in the difficulty of securing the electron transfers from the halide ion to carbon and thence to the displaced halogen atom, than to effects of entropy, *i.e.*, to differences in the mass, shape, and stiffness of the reacting system, including its solvation shell. This is consistent with our preconception that the halogens are closely grouped in polarity.

For the purpose of considering the variations of reaction rate which occur when the halogens are kept the same whilst the alkyl group is varied, it is convenient to work with Table 20, in which the rates are re-expressed on a relative basis: for each type of Finkelstein substitution, the rate of the reaction of the ethyl group is taken as the unit, ethyl being chosen because it is the one group which is common to both the α - and the β -methylated homologous series.

TABLE 20. *Found relative rates of Finkelstein substitutions in acetone at 25°.*

R	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	neoPe
(1) Cl ⁻ + RCl	71	1	—	—	—	—	—
(2) Cl ⁻ + RBr	61	1	0.013	0.0029	0.65	0.15	0.000026
(3) Cl ⁻ + RI	11	1	0.032	—	0.58	0.038	0.000014
(4) Br ⁻ + RBr	76	1	0.011	0.0030	0.65	0.033	0.000015
(5) Br ⁻ + RI	18	1	0.025	—	0.71	0.021	—
(6) I ⁻ + RBr	140	1	0.0078	0.0051	0.82	0.036	0.000012
(7) I ⁻ + RI	—	1	0.0088	0.0030	—	—	0.000018

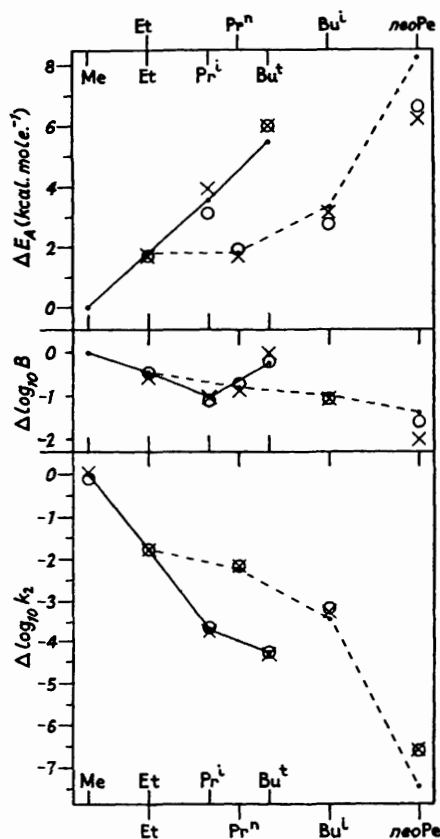
The picture here is of a fall of rate along the α -series, Me, Et, Prⁱ, Bu^t, in two moderate steps, followed by a third much smaller one; and of a fall along the β -series, Et, Prⁿ, Buⁱ, neoPe, in steps which grow successively steeper with rising intensity. The preceding discussion shows that, in the α -series, the smallness of the third step is due to the sudden restoration of the original symmetry at the end of the series, a restoration which superposes an entropic factor of steric acceleration on a ponderal entropy factor of retardation, and on the still-growing energetic factor of combined polar and steric retardation. We have seen also that, along the β -series, the entropy change alone accounts for the first small step, whilst entropy and energy effects both contribute to the succeeding steps, the last of which illustrates the characteristically sudden way in which steric hindrance becomes important, by reason of its energetic factor, as congestion in the system is progressively increased.

* The one apparent anomaly would undoubtedly disappear if salt conditions could be standardised down the columns of the Table, as they are along its rows (*cf.* p. 3224).

(b) *Calculated Structural Effects on the Rates of Finkelstein Substitutions and their Comparison with Observed Reaction Rates.*—Going beyond a qualitative description of the involved factors, as in the preceding paragraph, our discussions of Sections C and D solve quantitatively (though not with all the precision we would like) the two parts of the problem of accounting for structural effects on the rates of our reactions. And so it is of interest to put these parts together, and to see how closely their combination matches the experimental observations.

This synthesis and comparison is made comprehensively in Fig. 4, in which the scales of ΔE_A , $\Delta \log_{10} B$, and $\Delta \log k_2^{25}$ are so adjusted as to show directly the relative importance of the variations of activation energy and of frequency factor in the determination of the

FIG. 4. Calculated and observed effects of alkyl structure on the rates, and their energetic and entropic factors, of Finkelstein substitutions. In each part of the diagram, the same vertical height (apart from sign) corresponds to the same change in the free-energy of activation. The lines are theoretical: they join calculated points for the bromine-exchange reaction, and also the practically coincident points representing average values calculated for the seven Finkelstein substitutions. The points marked \times denote the observed values for the bromine-exchange, and those marked \circ represent means of observed values for all the substitutions.



rate relations. We can at present give theoretical rate values accurately and completely only for the bromine-exchange reaction, for which alone the entropy calculations have been finished: calculated frequency factors from Table 18, and calculated energy increments from Table 9, are combined in the Arrhenius equation. However, we can make similar, though only approximate, rate calculations for all the Finkelstein substitutions, employing throughout the entropy values calculated for the bromine exchange, and using, for the three symmetrical substitutions, the directly calculated energy values, and for the four unsymmetrical substitutions, energies interpolated as well as may be between the fairly close-lying values calculated for the symmetrical reactions. Most of the figures fall into such close groups that it is not possible to represent them all in one diagram; and therefore Fig. 4 compares, for each alkyl group, first, the calculated with the experimental values for the bromine-exchange reaction, and, secondly, the averages of the calculated values for all the seven reactions with the averages of all the available observed values for these reactions. The lines join points calculated for the bromine exchange; and equally they

join the points which represent the averages of calculated values, these points falling too close to the others to be shown separately. About these dual-purpose theoretical lines are entered the two sets of observational points, for which the data come from Tables 11, 6, and 20: one set is for the bromine exchange, whilst the other represents means of the observations made on all reactions of the series.

For closer assessment of the numerical performance of the theory in the calculation of structural effects on rate, Table 21 is given, in which calculated relative rates for the bromine-exchange reactions are compared with the corresponding observational values, derived from the figures in Table 19. It will be seen that the calculated rate figures are good to a factor of 2.5 over that range, 23,000, of rates which excludes the *neopentyl* group, and to a factor of 5.5 over the complete range of 5,000,000 which includes that group, certainly the worst-treated group of any by the approximations we have had to make.

TABLE 21. *Comparison of observed and calculated effects of alkyl structure on the relative rates at 25° of Finkelstein bromine-exchange in acetone.*

R:	Me	Et	Pr ⁱ	Bu ^t	Pr ⁿ	Bu ⁱ	<i>neo</i> Pe
Obs.	1	0.013	0.00014	0.000039	0.0085	0.00044	0.00000020
Calc.	1	0.017	0.00035	0.000053	0.0090	0.00035	0.000000037

When we make similar but approximate calculations as indicated above, for the other Finkelstein substitutions, so covering 49 reactions in all, and compare the results, where possible, with experiment, the degree of agreement is quite similar. There is no point in quoting these figures here, as they are bound to be changed to some extent by the further calculations now in progress; but it is already clear that structural effects on reaction rate can be approximately calculated in large numbers from a known mechanism with a minimum of dependence on the kinetic observations themselves. In the present calculations we use only one disposable constant for the whole assembly of groups and reactions.

It will be obvious that the theoretical analysis which has been illustrated here for the bimolecular nucleophilic exchange of halogens, could be extended to any bimolecular nucleophilic substitutions at saturated carbon. The main complication in practice would be that, for a polyatomic substituting agent, or a polyatomic displaced group, it would be necessary to estimate, as could certainly be done in a rough way, the bending potentials at the outward ends of the semi-bonds of the transition state, and, proceeding by successive approximations, to allow these potentials to adjust transition-state configurations at first calculated without them.

It is obvious, too, that the method of analysis illustrated could be paralleled for some quite different types of reaction, provided, of course, that the mechanism is sufficiently well known to enable an electronic and geometrical description of its transition state to be given. The main significance of the present work may be that it indicates the nature and feasibility of the next step, which becomes possible when a reaction mechanism has been elucidated thus far.

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