

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, NEWARK, DEL.]

Evaluation of the Relative Importance of Charge-Dipole Interactions and Steric Strain Acceleration in Conformationally Mobile Systems

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The relationship (eq. 1), now known as the W-H equation,³ has been applied previously^{2,3} on the basic assumption that the solvolysis reaction of a 4-*t*-butylcyclohexyl tosylate has the same transition state as the corresponding unsubstituted (axial or equatorial) structure. A number of different data have been arrayed here in support of the contention that this assumption is incorrect, and that the W-H analysis of tosylate solvolysis consequently breaks down. Contrary to this widely applied premise,³ it has been concluded that the rate effect of a 4-substituent in cyclohexyl tosylate acetolysis is *not solely* a measure of the intrinsic difference between the equatorial and axial orientations of the tosylate group. A linear free energy relationship has been shown to correlate with fair precision both the steric strain acceleration and polar interaction factors that arise from the presence of a 4-substituent in cyclohexyl tosylate solvolysis. The dominant importance of the polar interaction factor controlling the rates of solvolysis in cases of highly polar 4-substituents and the somewhat greater influence of the *cis* vs. the *trans* substituent ($\rho_e > \rho_t$) have been noted and have received detailed consideration. The significance that these results hold for the structure of the solvolytic activated states of the diastereomeric tosylates has also been discussed and the inference tentatively deduced that the *cis* series members react in a twist-boat (conformation) transition state while the *trans* have the usual chair.

Reactivity in mobile cyclohexyl systems has been extensively subjected to conformation analysis.^{2,3} The ratios of reaction rates of *cis* and *trans* isomers have been correlated with their respective ground state conformational preferences on the basis of the explicit assumption that the remote substituent used as the reference for this analysis exerts no polar influence at the reaction site.

The kinetic analysis originally due to Winstein and Holness^{3,4} has been elaborated in a recent text.⁵ These

authors have advocated by means of such reaction schemes as Fig. 1 that (for example) the course of solvolysis of cyclohexyl tosylates follows the unbroken arrows in the diagram shown. The formation of products, to all intents and purposes, was assumed to have *only* two routes, k_A and k_E , leading, respectively, from the axial (A) and equatorial (E) conformations of the tosylate. The paths we have indicated by means of the dotted line $k_{A'}$ and $k_{E'}$ were essentially disregarded.

Winstein and Holness have concluded that eq. 1 and 2 are identical and there is no necessity for considering the cross over implied by eq. 2 (apparently) by the following line of reasoning, which can be perceived with the aid of the energy diagram in Fig. 1. (a) The amount of material going from states $E \rightarrow E^\ddagger$ is independent of the path taken; *i.e.*, it is the same whether the path is $E \rightleftharpoons A \rightarrow E^\ddagger$, or $E \rightarrow E^\ddagger$. A similar assumption is made for $A \rightarrow A^\ddagger$. (b) The rates of reaction leading from E, *i.e.*, attainment of transition state E^\ddagger , are the same for all possible paths. (c) The number of paths available for the conversion of E to E^\ddagger do not influence the over-all rate of conversion.

On the basis of these assumptions it can be readily seen

$$k_E N_E = k_{E'} N_A \quad (4)$$

$$k_A N_A = k_{A'} N_E \quad (5)$$

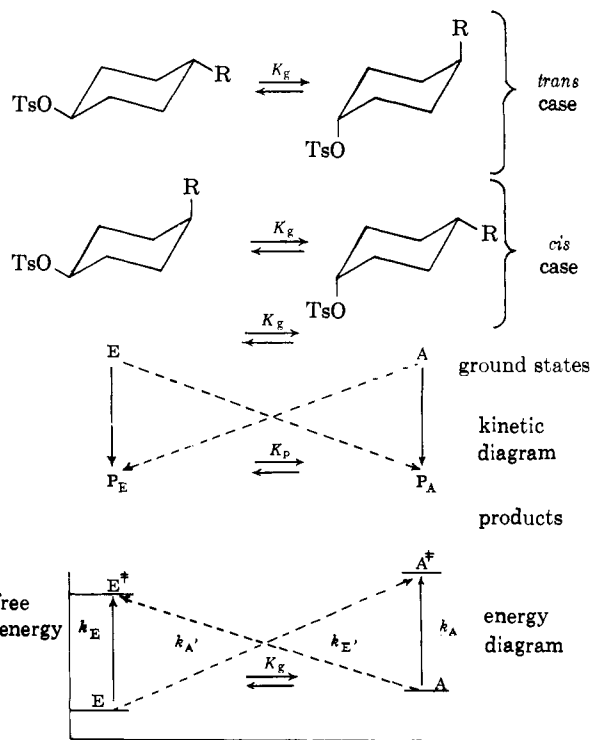
and also

$$\text{total rate} = \frac{1}{2}(k_E N_E + k_{E'} N_A + k_A N_A + k_{A'} N_E) \quad (6)$$

and, on substituting eq. 4 and 5 into 6, one gets the W-H eq. 1. It is asserted on this basis that the W-H equation is always true and it makes no difference whether material starts from the axial conformation and goes directly to the transition state or whether it goes first to the equatorial ground state and thence to the axial transition state.

But, is the W-H equation always applicable? In particular, does it apply when we are comparing 4-*t*-butylcyclohexyl with the corresponding unsubstituted derivatives? It is our contention, in fact, that it *does not apply* for the very comparison on the basis of which Winstein, Holness,³ and Eliel and Ro² have actually computed *A*-values with the readily derived eq. 3. Our argument in support of this contention is as follows.

The most direct argument against the W-H hypothesis is the fact that it doesn't fulfill prediction. It predicts, for example, that determination of the *A*-value³ (where *A* is the ground state free energy dif-



$$k = k_E N_E + k_A N_A; \text{ ignoring cross over} \quad (1)$$

$$k = (k_E + k_{A'}) N_E + (k_A + k_{E'}) N_A; \text{ taking cross over into account} \quad (2)$$

$$A = RT \ln \frac{N_E}{N_A} = RT \ln \frac{k_A - k}{k - k_{E'}}; \text{ Winstein-Holness relation for calculating conformational free energy differences} \quad (3)$$

Figure 1.

(1) Fulbright Fellow at the University of Delaware, 1959-1962.

(2) E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).(3) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).(4) See also E. L. Eliel and R. S. Ro, *Chem. Ind. (London)*, 251 (1956).

(5) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 234 ff.

ferences between axial and equatorial conformers as calculated according to the derived³ expression of eq. 3) should be independent of the nature of the reaction transition state in which cyclohexyl and 4-*t*-butylcyclohexyl tosylates are being compared. That is to say, we should expect A for the tosyl group to be the same without consideration of the reaction kinetics from which it can be estimated by applying the W-H eq. 3. That this is not the case can be seen from a number of data. For instance, for the unimolecular tosylate solvolysis in acetic acid, the value of the tosyl group is reported² to be $A = 1.7$ kcal. (apparently a nearly temperature-independent quantity).³ On the other hand, the purportedly identical quantity determined by measurement of bimolecular tosylate displacement and elimination rates with both thiolate and alkoxide anions is given⁵ as $A = 0.7$ kcal. at 25°

A second experimental failure of the W-H hypothesis can be realized by examination of the activation parameters determined for cyclohexyl tosylate solvolysis. If the unsubstituted cyclohexyl tosylate solvolyzes *via* two transition states (axial and equatorial), which are assumed³ to be respectively identical with the *cis*- and *trans*-4-*t*-butyl, we should expect its activation parameters to be intermediate between those of the axial and equatorial transition states of reference. The validity of the W-H hypothesis is seen to rest squarely upon this expectation. Instead, it is found that cyclohexyl tosylate solvolyzes in formic acid with activation parameters ($\Delta H^\ddagger = 23.8$ kcal., $\Delta S^\ddagger = +1.0$ e.u.) which are definitely outside of the limits delineated by those of *cis*- ($\Delta H^\ddagger = 22.0$, $\Delta S^\ddagger = -2.4$) and *trans*- ($\Delta H^\ddagger = 22.9$, $\Delta S^\ddagger = -2.0$) 4-*t*-butyl, the latter (two) sets being, in fact, closer to each other than to the former with which they are to be compared. It will be readily seen, also, that the reaction rate constant, k , for cyclohexyl tosylate will be intermediate between those of the *cis*- and *trans*-4-*t*-butyl tosylates *only* in a relatively narrow temperature range. At the ends of this range, the unsubstituted case will have a (respectively) greater or smaller k .

A variety of evidence at hand, both theoretical and experimental, provides additional grounds for suspecting that the activated states for reactions of the 4-*t*-butyl derivatives are not to be equated, respectively, with the unsubstituted cases, as has been assumed in the W-H hypothesis. These lines of evidence indicate that a bulky substituent, such as the *t*-butyl group, would introduce distortions in ground state bond angles and reduce the normal flexibility of the unsubstituted cyclohexane ring. Thus, Westheimer⁶ has inferred that all sorts of steric interactions produced by substitutions of this nature find some relief in distortion of normal bond angles, since the energetic requirements for such deformations are smaller than the steric interaction energies so relieved. Furthermore, recent studies⁷ of the ground state conformations of alkyl substituted cyclohexanols based on infrared and n.m.r. data suggest that rapid conformational interconversion (flexibility) is considerably diminished by remote substitution of bulky groups on the ring.

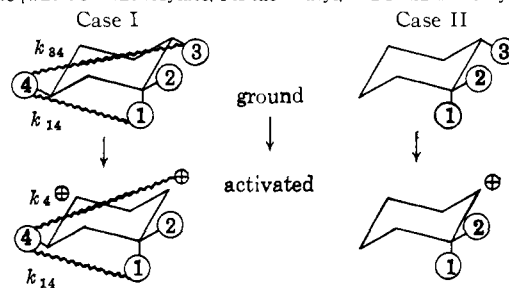
Angular distortions and decreased flexibility of the ground state may thus be considered to have similar origins in increased steric interactions occasioned by substitution of hydrogen with *t*-butyl. These ground state effects, we believe, reflect themselves to a pronounced extent in the activated states of the solvolytic

reactions being compared in the W-H hypothesis.^{8b} This conclusion can be readily reached by means of the statistical mechanical treatment given in Mayer's textbook^{8a} on the subject. In this analysis the free energy of the transition state can be expressed as the sum of the zero point free energy and $RT \ln V$, where V is the configuration integral. This amounts to the products of the volumes available to each atom weighted for the time spent in each position in space. The positions available to the leaving group (tosylate anion) are considerably more limited in the *t*-butyl than in unsubstituted cyclohexyl. That is to say, the fluctuations in position of the leaving group due to thermal energy (in the direction of interconverting axial and equatorial forms) will be highly restricted in the case of *t*-butyl because of the (apparently) vastly lower energy of the equatorial position of this group. Consequently, the free energies of the transition states of the 4-*t*-butyl and unsubstituted cases will be considerably different,^{8b} in contradiction to the assumption of the W-H hypothesis.

Some interesting examples demonstrating that the activation parameters of the axial and equatorial tosylate solvolysis transition states differ significantly, as a result of remote substitution of alkyl groups on the ring, are given by the following data comparison.

In the ground states a tosylate group in the diastereoisomers being compared in Table I is considered to be "fixed" in either the axial or equatorial conformation. If (as the W-H hypothesis has assumed³) the observed

(8) (a) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 213-217. (b) A referee has claimed that no difference between the ΔS^\ddagger for the substituted or unsubstituted case would be anticipated, since there is no more nor less freedom in the transition state *relative* to the ground state in the cyclohexyl than in the *t*-butyl case. The referee's assumption here, however, can be shown to be untenable on the basis of the following straightforward analysis: Let us assume, for the moment, that ΔH^\ddagger is the same for the 4-*t*-butyl solvolysis (II) and the unsubstituted cyclohexyl solvolysis (I). Therefore, ΔS^\ddagger is the quantity of interest determining the ΔF^\ddagger for the transition from ground to activated states for I and II. Recognizing that the entropy is a quantity which is a measure of the order or disorder that is characteristic of the configurations being compared, it is possible to consider several comparisons of I and II by means of a conventional model of the equatorial tosylate [where 3 is the tosylate, 4 is the *t*-butyl, and 1 and 2 are hydrogens].



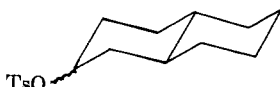
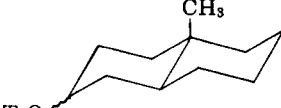
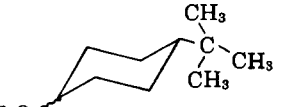
The same referee has conceded and experience tells us that the ground states of case I and II are significantly different as to flexibility.⁷ This undoubtedly must be attributed to interactions between the *t*-butyl group and the tosylate group as well as with the ring hydrogens 1 and 2 in case I, that are absent in case II. Such interactions are both steric and of the nature of potential field interactions which regulate the motions of the groups with respect to each other. These restraints may be approximated in the model by springs of varying force constants k between relevant groups. Thus the ground state of I will be that much less flexible than II (for example) by virtue of interactions that can be designated by k_{14} and k_{24} and absent in II. On reaching the transition state, k_{24} will tend to disappear and in its place another interaction, $k_{4\oplus}$, will develop. Furthermore, the k_{14} 's will also be strongly altered by the developing carbonium ion center, \oplus , in the transition states. Clearly, $(\Delta S^\ddagger)_I$ will depend upon the loss of the k_{24} , the appearance of $k_{4\oplus}$, and the modification of the k_{14} 's. For these reasons, it is obvious, $(\Delta S^\ddagger)_I - (\Delta S^\ddagger)_{II} \neq 0$. Consequently, we infer that a significant difference in both steric and potential field interaction change in going from ground to transition state will generally distinguish cases I and II. The failure of the W-H equation to give experimentally consistent results, as pointed out in our discussion above, necessarily compels the conclusion that $(\Delta F^\ddagger)_I - (\Delta F^\ddagger)_{II} \neq 0$. This disparity in free energy correlates most reasonably with the occurrence of a $\Delta(\Delta S^\ddagger)$ term, in contradiction to the assumptions on which the W-H equation has been applied.

(6) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12, and references cited therein.

(7) H. Finegold and H. Kwart, *J. Org. Chem.*, **27**, 2361 (1962).

TABLE I

SOME RATE DATA FOR ACETOLYSIS OF SUBSTITUTED CYCLOHEXYL TOSYLATES WITH CONFORMATIONALLY RELATED GROUND STATES

| Tosylate |  | | |  | | |  | | |
|-------------------------------------|---|--------|------|--|--------|------|---|--------|------|
| | Axial | Equat. | Ref. | Axial | Equat. | Ref. | Axial | Equat. | Ref. |
| $10^5 k$, sec. ⁻¹ , 75° | 6.19 | 1.99 | 9a | 16.0 | 2.62 | 9b | 10.2 | 3.62 | 3 |
| Rel. rate ^a | 1.7 | 0.55 | | 4.4 | 0.72 | | 2.8 | 1.0 | |
| ΔH^\ddagger , kcal. | 27.8 | 28.5 | | .. | .. | | 26.7 | 28.1 | |
| ΔS^\ddagger , e.u. | -1.8 | -1.6 | | .. | .. | | -0.5 | +1.7 | |

^a Based on *trans*-4-*t*-butylcyclohexyl tosylate.

rates are related to the conformational distribution in the ground states, and the rates tend to be solely a measure of the intrinsic difference between the equatorial and axial positions of the reactive group on the cyclohexane ring (which is the basis on which the free energy differences between group conformations are calculated).^{2,3} we must expect a close correspondence of the rates and activation parameters of all the corresponding epimers in Table I. This expectation is obviously not borne out by the data.

The investigators who have studied the fused ring tosylate acetolysis reactions have consistently advanced cogent arguments attributing the rate factor resulting from introduction of the angular methyl group to steric interactions with the 1,3-diaxial hydrogens.⁹ Similar effects must exist, too, for the comparable 4-*t*-butylcyclohexyl derivative. Clearly, these interactions are present in both the ground and activated states. It is just as clear, also, that these effects are not cancelled out in considering the ratio of rates of two diastereomeric substances, as had been anticipated.³ The data in Table I must be taken as direct experimental evidence (supporting the model analysis offered above^{8b}) against the contention that there is no more or less freedom in the transition state relative to the ground state in cases which differ only in the degree of remote alkyl substitution on the ring.

As stated earlier, Winstein and Holness³ and Eliel² have explicitly assumed that the *t*-butyl group is so distant from the reaction zone in which the tosylate is ionizing that its polar effect will be negligible. This may indeed be one of the unwarranted assumptions upon which the W-H hypothesis stumbles. We submit, however, that the data and arguments we have reviewed above make it appear also likely that various subtle influences arising from steric distortions and potential field interactions that restrain motion in the 4-substituted cyclohexyl derivative will always tend to alter its transition state structure sufficiently to render it unfit for comparison with the corresponding unsubstituted derivative, within the context of applying the W-H hypothesis. In sum, we wish to emphasize the likelihood that the presence of any substituent (even *t*-butyl) at the 4-position of the cyclohexane ring can result in charge-dipole interactions that will modify not only the structure of the ring, but also the charge at the seat of reaction. We propose to develop this point further in the following sections.

A Basis for Interpreting the Effect of Remote *cis* and *trans* Substituents in Cyclohexyl Tosylate Solvolysis.—To account for the observed rate difference between *cis*- and *trans*-4-*t*-butylcyclohexyl tosylates in solvolysis, we initially make the very reasonable assumption (also made earlier^{2,3}) that the *t*-butyl substituent regulates both the ground and transition state orientations of the

tosylate group in both the *cis* and *trans* isomers. In general, as we change the nature and size of the 4-substituent we must certainly expect variation in the conformational composition of the ground state. However, since in the transition state for solvolysis a considerable extent of elongation of the ring carbon-tosylate bond has occurred, the 4-substituent usually tends to become much more effective in controlling conformation in the transition state. (This is especially true if solvation change has not significantly entered into determination of conformational disposition.) Again, in accompaniment to the ionization of the carbon-tosylate bond, we experience a steep increase in the energy of electrostatic interaction with the remote 4-substituent dipole.

It will be evident, therefore, that several factors govern the rate of tosylate solvolysis which can be related to the conformational and polar influences of the 4-substituent. The inherent rate effect due to conformation correlates with the magnitude of the repulsive interactions relieved in attaining the carbonium ion transition state. The size of the polar influence on rate may be related to the amount of charge developed at the seat of ionization in the transition state and its interaction with the dipole of the 4-substituent. Classically, the polar interaction energy will vary inversely with (some power of) the distance of separation of charge and dipole, the orientation of the dipole, and the dielectric of the intervening medium. It will also be seen that such polar interaction energy, if sufficiently large, may contribute to determining the transition state conformation (and *vice versa*) and, in a second-order fashion, therefore, the magnitude of the rate effect due to repulsive interactions relieved in the transition state. This follows from the expectation that a sufficiently large charge and a dipole placed (respectively) at the 1 and 4 ends of the cyclohexane ring will effect some bending of the ring in the direction of increased interaction even at the expense of increased steric strains in the ring structure.

We can anticipate on this basis that a series of *cis*-4-substituted cyclohexyl tosylates, where the dimensions of the 4-substituent dipole exceed some threshold value, will possess similar transition state conformations. An analogous statement applies for a *trans* series. The occurrence for each series of a linear free energy relationship encompassing considerable regularity of polar and steric terms might therefore be expected; *i.e.*, $\log k_R$ in each series is a function of both the polar interaction and steric strain free energy change in going to the transition state and, in the unsubstituted case ($R = H$), the transition state will resemble that of the *trans*-tosylates. All these circumstances may be expressed by eq. 7, 8, and 9

$$\log k_c = \rho_c \sigma_1 + (\Delta F_c/RT) + C \quad (7)$$

$$\log k_t = \rho_t \sigma_1 + (\Delta F_t/RT) + C \quad (8)$$

$$\log k_H = \rho_H \sigma_1 + (\Delta F_H/RT) + C \quad (9)$$

(9) (a) I. Moritani, S. Nishida, and M. Murakami, *J. Am. Chem. Soc.*, **81**, 3420 (1959); (b) S. Nishida, *ibid.*, **82**, 4290 (1960).

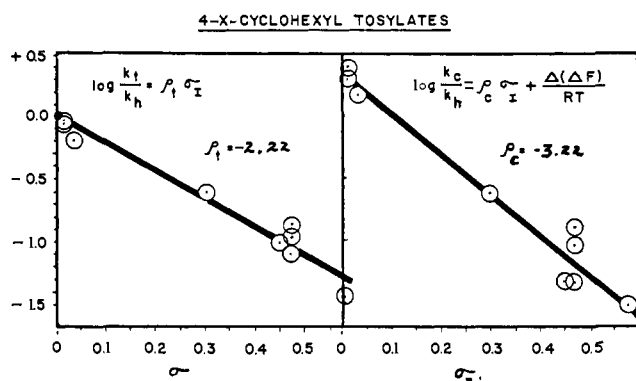


Fig. 2.—Linear free energy plots; solvolysis of *trans*- and *cis*-4-X-cyclohexyl tosylates.

where the subscript *c* denotes the corresponding parameters of the *cis* series and *t* of the *trans* series. The familiar $\rho\sigma$ term measures the free energy of inductive and field interaction¹⁰ and each $\Delta F/RT$ term is an estimate of the steric strain and repulsive interaction energies released in achieving the activated state.¹¹ The unspecified constant term *C* is assumed to have the same value in both series and can be eliminated as follows.

Since σ_I for *H* is exactly equal to zero, eq. 9 reduces to $C = \log k_H - (\Delta F_t/RT)$. Substituting this into eq. 7 and 8 gives

$$\log \frac{k_c}{k_H} = \rho_c \sigma_I + \frac{\Delta F_c - \Delta F_t}{RT} \quad (10)$$

$$\log (k_t/k_H) = \rho_t \sigma_I \quad (11)$$

These equations predict that the rates of *cis* substituted cases will comprise a line whose slope is a direct measure of the magnitude of polar interaction in the *cis* transition state for solvolysis and whose intercept provides an estimate of the difference in steric strain released compared to that of the *trans* as the reference transition state. The rates of the *trans* series are anticipated to comprise a second line whose intercept passes through zero. The extent to which members of the series adhere to the predicted lines constitutes a test of the basic assumption of a similarity in transition state structure.

Results and Discussion

To determine the extent to which the above treatment is applicable, we have measured the rates of solvolysis in glacial acetic acid at *ca.* 75° of a series of 4-substituted cyclohexyl tosylates in both the *cis* and *trans* relationships. The data obtained are summarized in Table II with similar data reported by Noyce and co-workers¹² at 90°.

All these data have been plotted according to the linear free energy (LFE) relationships (eq. 10 and 11) in Fig. 2. The validity of the assumptions made in this analysis can now be examined in the light of these data. We may first note that the correlating straight lines accommodate the data of $\log k_R/k_H$ at both 75 and 90°. This is predictable from eq. 10 and 11 where the temperature dependence (directly) appears only in the steric factor and where a 15° rise in the absolute

temperature corresponds at most to a 5% reduction in the magnitude of this term. Apparently the dependence of ρ_c and ρ_t on temperature is not great in the range of interest here.

The fact that the unsubstituted case (*H*) falls on the *trans* series line and is most remote from the *cis* is consistent with the postulate that its activated state has the equatorial tosylate exclusively. The difference in the intercepts of the two lines is a direct evaluation of the steric strain acceleration¹⁰ factor that enhances the solvolysis in the axial (*vs.* the equatorial) tosylate by almost 600 cal.

TABLE II
RATES OF ACETOLYSIS OF *cis*- AND *trans*-4-SUBSTITUTED
CYCLOHEXYL TOSYLATES

| 4-Subst. | Temp., °C. | <i>cis</i> | | <i>trans</i> | | σ_1^b |
|-----------------------------------|---------------|--|---------------------|--|------------------|--------------|
| | | k_R , sec. ⁻¹ × 10 ⁶ | log k_R/k_H | k_R , sec. ⁻¹ × 10 ⁵ | log k_R/k_H | |
| -H | 75.7 ± 0.1 | ... | ... | 5.28 | 0 | 0 |
| -CH ₃ | 75.7 ± .1 | 7.83 | +0.17 | 3.24 | -0.21 | 0.03 |
| - <i>t</i> -Butyl | 75.0 ± .1 | ... | + .393 ^a | ... | - .041 | .016 |
| -COOC ₂ H ₅ | 75.7 ± .1 | 1.30 | - .61 | 1.28 | - .616 | .30 |
| -Cl | 75.7 ± .1 | 0.67 | - .897 | 0.41 | - 1.11 | .47 |
| -OCOC ₂ H ₅ | 75.7 ± .1 | 0.50 | - 1.02 | 0.74 | - 0.86 | .47 |
| -H | 90° | ... | ... | 26.5 | 0 | 0 |
| -Cl | 90 | 1.21 | - 1.34 | 2.85 | - 0.96 | 0.47 |
| -Br | 90 | 1.21 | - 1.34 | 2.43 | - 1.03 | .45 |
| -CN | 90 | 0.81 | - 1.51 | 0.93 | - 1.45 | .58 |
| - <i>t</i> -Butyl | 90 | ... | + 0.30 | ... | - 0.05 | .016 |

^a Values calculated from data given in ref. 3. ^b Values obtained from ref. 12. ^c Data measured at 90° taken from ref. 10, 14, and 15.

Summary: The parameters of the least square lines (see Fig. 2) plotted from the data in this table were determined by the usual statistical methods. Appropriate definitions of the statistical symbols used below are well discussed by W. F. Ames, *Textile Res. J.*, **32**, 8 (1962), and by C. A. Bennett and N. F. Franklin, "Statistical Analysis in Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1954.

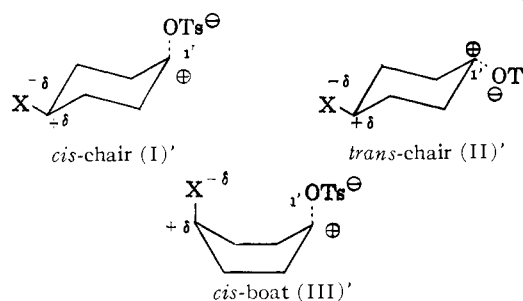
$\log (k_c/k_H) = -3.22\sigma_1 + 0.35$ (multiple correlation coefficient); $r = 0.986$

$$\log (k_t/k_H) = -2.22\sigma_1; r = 0.992$$

The *F* test for eq. 10 gave a value of 28 and for eq. 11 a value of 51. Since for both cases a value of *ca.* 16 is all that is necessary for significance at the 0.25% level, it will be recognized by means of these statistical criteria that more than "highly significant" correlations have been established for eq. 10 and 11.

We note also that the smaller groups (Cl, CH₃, CN, etc.) fall on the small plot as the larger groups (*t*-butyl, carboxy). If the rate differences between corresponding *cis* and *trans* cases were independent of the nature of the transition state and depended solely on the conformational preferences in the ground state determined by a remote substituent,^{2,3} we could scarcely have predicted that groups of such very different size and polar influence could be correlated by eq. 10 and 11.

The occurrence of two different lines (Fig. 2), one for each of the respective *cis* and *trans* series, suggests that the isomeric transition states differ considerably in the degree of charge-dipole interaction. If both series of reactants passed through transition states in the chair conformation, we would have anticipated that the *trans* isomer series would exhibit the greater



(10) See for examples (a) H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961); and (b) H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962).

(11) The inference of steric strain acceleration in solvolysis reactions have been extensively discussed elsewhere. See for examples, P. D. Bartlett, *J. Chem. Educ.*, **30**, 22 (1953); A. Streitwieser, Jr., *Chem. Rev.*, **56**, 709 (1956); H. C. Brown, *Science*, **103**, 385 (1946).

(12) D. S. Noyce, B. N. Bastian, and R. N. Monson, *Tetrahedron Letters*, 863 (1962). We are obliged to Dr. Noyce for the opportunity to study this data (on Dec. 1, 1962) before the appearance of his communication.

sensitivity to 4-polar substitution. In this connection some direct computations of coulombic interaction energies are very informative. Thus, we find that at all distances (l') of extension of the $\geq\text{C}-\text{OTs}$ bond, undergoing ionization in the transition state, both *cis* (I)' and *trans* (II)' chair conformations result in repulsive interactions. The corresponding *cis*-boat (III)' conformation experiences an increasingly attractive interaction as the departing tosylate becomes separated from the ring by about nine times its ground state covalent bond distance.

The simplest explanation, therefore, of the greater response to 4-polar substitution in the *cis* series requires here that the transition state ionization occur in the boat conformation. While this conformation is attainable only through the expense of energy in folding the ground state chair, a vastly greater degree of charge-dipole interaction is allowed to develop. In all probability, too, a modification of the boat, discussed by Hendrickson¹³ (among others) as the twist-boat, is the most appropriate description of the activated state of the ring. Here nonbonded interactions between substituents on adjacent carbons have been minimized and the energy requirement for its formation diminished correspondingly. There is still permitted, however, a degree of dipolar interaction nearly equal to that experienced in the fully formed boat between the *cis*-4-substituent and the charges developing at the seat of reaction. Furthermore, the *trans* series members probably react in a chair conformation transition state, since approximate calculations create serious doubt that greater interaction energy can be realized in the *trans*-boat or any conformation resembling it. It is somewhat doubtful, too (although not completely improbable), that the methyl and *t*-butyl dipoles which are of very small magnitude can exert sufficient effect even in the *cis* case to produce interaction energies sufficient to repay the energy expended to fashion the twist-boat transition state. If this is so, however, using the familiar Taft σ_1 -values¹⁴ for these groups will result in departures from the *cis* line, as we have observed earlier.¹⁰ We have therefore used the modified σ_1 -values determined from our earlier data in analogous reaction series.¹⁰

This brings up the question of the choice of the "type" of substituent constants to use, among a variety that are available for application in the plots of Fig. 2. This was not considered to be crucial since no direct significance has been (here) attached to the absolute magnitudes of the ρ -values (so determined). As far as the quality of fit to a straight line relationship was concerned, it did not matter whether we employed the σ -values of Roberts and Moreland¹⁵ as elaborated by Taft and Lewis¹⁴ or the constants deduced by Siegel and Komarmy¹⁶ from measurement of the influence of *trans*-4-substituents on the acidity of cyclohexanecarboxylic acids. Taft and Lewis¹⁴ have compiled a list of σ -values that are directly proportional to the corresponding Roberts and Moreland values, though about 30% lower. Furthermore, we have used σ_1 -values¹⁴ earlier¹⁰ to demonstrate the polar effects of remote transannular substituents on the rates of addition to the double bond in a reaction series of substituted cyclohexenes. Consequently, some confidence in the application of such σ_1 -values (employed for Fig. 2) would seemingly be realized by comparison

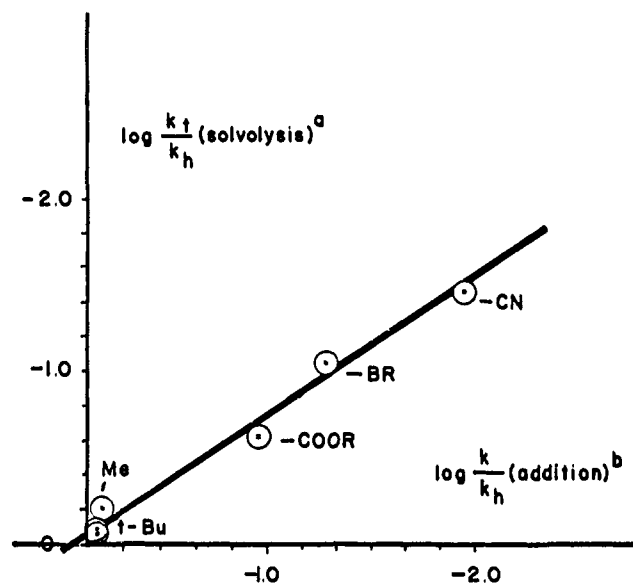


Fig. 3.—Linearity of rates of solvolysis and double bond addition reactions regulated by remote polar substituents. ^a Data listed in Table I. ^b Data taken from ref. 9a.

of the relative rates of the addition reactions with the corresponding quantities we have measured for solvolytic series of *trans*-4X-cyclohexyl tosylates, where (again) we are assuming that only the *polar* effect of the transannular substituent is regulating the rate (*cf.* eq. 11). The plot presented in Fig. 3 suggests, indeed, that the factors of substitution controlling the rates in these reactions are fairly similar and provides a substantial basis for using the same σ_1 -values for tosylate solvolysis that now appear to be applicable in a number of other cases.^{10,14}

We can anticipate that a question may be raised concerning our observation that methyl and *t*-butyl have weakly electron withdrawing substituent constants. The σ_1 -values listed by Taft and Lewis¹⁴ have been determined by a process of sorting out the inductive and resonance components of the substituent effect in *meta* and *para* aromatic side chain reaction series, according to the empirical equation

$$\log (k^m/k_0) - \alpha \log (k^p/k_0) = \sigma_1(\rho_1^m - \alpha\rho_1^p)$$

These values have been correlated in a few cases with the σ' -values of Roberts¹⁵ by means of another empirical relation, $\sigma_x' = 0.45\sigma_{\text{XCH}_2}$. However, none of the previous authors¹⁴⁻¹⁶ have ever measured a σ_1 -value directly on a methyl or *t*-butyl group which was separated from the reaction center by more than two $-\text{C}-\text{C}-$ σ -bonds, the substituent relationship in a purely aliphatic (nonaromatic) reaction series. Consequently, the available σ_1 -values¹⁴ for methyl and *t*-butyl have been computed from cases in which very small substituent effects on rate or equilibrium has been deduced—but never directly determined—as the small residue after one has presumably subtracted away resonance and steric effects from the total of all these effects that can exert control on the magnitude of the substituent influence. There is, in fact, no direct measurement which would indicate that a remote methyl or *t*-butyl group separated from the seat of reaction by at least four C-C bonds would exert an electron-releasing effect, as presumed from the σ_1 -values assigned.¹⁴

It should be perfectly clear, however, that regardless of whether we use the original $\sigma_1 = -0.05$ and -0.07 (respectively) for methyl and *t*-butyl, or our directly determined¹⁰ ($\sigma_1 = +0.03$ and $+0.016$) values, there is no significant effect on the precision of the correla-

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tion we obtain, as expressed by the LFE equations 10 and 11. The *trans* reaction series line still passes through zero, *i.e.*, encompasses the unsubstituted case, and the *cis* reaction series constitutes an entirely different line with a considerable positive intercept. Furthermore, the conclusions we have drawn above with regard to the manner of the 4-substituent effect transmission (field effect) and the factor of steric strain acceleration in the rate of tosylate solvolysis are almost unaltered by our choice of available σ_1 -values for methyl and *t*-butyl.

However, our observations, here and previously,¹⁰ that the purely electrostatic influence of the alkyl group, conveyed as a field effect is weakly electron attractive invites some speculation as to its origin. It seems clear enough that the $-\text{CH}_3$ group is a complex dipole where $\mu(\text{C}^--\text{H}^+) = 1.53 \text{ D}$.¹⁷ The effect of the negative carbon pole depends for its conveyance to the reaction center on the nature of the atom to which it is bonded. That is to say, the magnitude of electron release experienced depends upon the apparatus available for its transmission from this atom. If this atom is trigonal and a constituent of a π -electron connection to the seat of reaction, the electron-releasing influence can be transmitted either by inductive polarization or mesomerically. On the other hand, it has been shown¹⁸ by means of nuclear quadrupole moment studies that when the negative end of the methyl dipole is attached to a tetrahedron carbon (*i.e.*, the 4-carbon of the cyclohexane ring), its electron release effect is completely damped out beyond two $-\text{C}-\text{C}$ -bond distances. Consequently, the positive pole of the methyl group, which is based on the hydrogen atoms on its periphery, and which must depend for its transmission on the total composition and nature of the transannular space, will manifest itself at the seat of reaction only if a sufficiently low dielectric medium is interposed. This is more likely to be the case where a cycloalkane ring, composed largely of hydrocarbon material, occupies the space between the positive periphery of the $-\text{CH}_3$ and the electric charge development at the reaction center in the transition state.

(17) For a full discussion of this see C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942).

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Experimental

Kinetic Measurements.—The general procedure recommended by Winstein and co-workers¹⁹ was followed in measuring the acetylation rates.

TABLE III
PROPERTIES OF 4-N-CYCLOHEXYL TOSYLATES

| 4-Substituent | Source | M.p., °C. | Lit. m.p., °C. |
|---|--------------|-----------|-----------------------|
| H- | ^a | 43-43.5 | 43.5-44 ²⁰ |
| <i>cis</i> -CH ₃ | ^b | 70-70.8 | 70-71 ²¹ |
| <i>trans</i> -CH ₃ | ^b | 71.5-71.9 | 71-72 ²¹ |
| <i>cis</i> -COOC ₂ H ₅ | ^c | 43-45 | |
| <i>trans</i> -COOC ₂ H ₅ | ^c | 69-69.5 | |
| <i>cis</i> -Cl | ^d | 43-44 | |
| <i>trans</i> -Cl | ^d | 74-75 | |
| <i>cis</i> -O-COC ₆ H ₅ | ^e | 86.5-87 | 94-95 ²² |
| <i>trans</i> -O-COC ₆ H ₅ | ^e | 150-151 | 150-151 ²² |

^a The cyclohexanol was obtained from Eastman, White Label. ^b Columbia Organic Chemicals, Columbia, S. C. ^c The *cis*-carboxycyclohexanol was prepared by the method of Noyce, *et al.*,²³ by lactone ring opening with NaOC_2H_5 ; b.p. 96-98° (0.7 mm.). The *trans*-4-hydroxy acid was prepared according to the method of Campbell and Hunt.²⁴ ^d The *trans*-4-chlorocyclohexanol was prepared in the manner of Bennett and Niemann²⁵ from the 1,4-oxide. The *cis* isomer was prepared by sodium borohydride reduction of 4-chlorocyclohexanone.^{9b} The crystallized *cis*-alcohol was analyzed by v.p.c. and the rate of the tosylate solvolysis corrected for the amount of *trans* isomer present. The mixed alcohol was tosylated, dried, and allowed to react without further purification to prevent unintentional fractionation. ^e The *cis*- and *trans*-4-benzoyloxy cyclohexanols were prepared by the method of Owens and Robins.²²

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[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY, ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Nuclear Magnetic Resonance Spectra of Some Norbornadienes and Norbornenes

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A study of the n.m.r. spectra of several 7-substituted norbornadienes and norbornenes has established several criteria for configurational assignment of the 7-substituent with respect to the double bond(s). These criteria are: (1) a long-range coupling constant of 0.8 c.p.s. is present between the bridge hydrogen and the vinyl hydrogens *anti* to it; (b) the sum of the vicinal and allylic coupling constants of the bridgehead proton with the vinyl protons is greater when *syn* to the bridge hydrogen than when *anti*; (c) the bridge hydrogen is more shielded when *syn* than when *anti* to the double bond. The relation between the presence of the aforementioned long-range coupling and delocalization of the bridge carbon orbitals is discussed with reference to the abnormally fast solvolytic reactions of the systems above. A simple LCAO-MO calculation for 7-ketonorbornene is presented.

In the course of an investigation of some aspects of the chemistry of 7-substituted norbornadienes and norbornenes, we have observed a stereospecific, long-range coupling constant between the ring vinyl hydrogens and the *anti*-7-hydrogen. This paper presents the pertinent observations and a discussion of their significance, both as related to simply determining the stereochemistry of 7-substituted norbornenes and to the larger problem of orbital interaction between the π -electron

system of the ring carbons and the orbital system at the 7-carbon.

N.m.r. Spectra.—Inspection of the 60 Mc. n.m.r. spectrum of several 7-substituted norbornadienes reveals a differing multiplicity of the two ring vinyl hydrogen patterns (Fig. 1). The vinyl multiplet occurring at lower field appears as a triplet or, more precisely, as a quartet whose inner members are separated by an amount sometimes outside of instrumental