not calculated the energy of the transition state, we cannot be certain, but it seems likely that the compound would not be stable at room temperature, but would spontaneously isomerize one or both of the linkages to the cis configuration.

Looking at Table IX, we see that *trans*-di-*tert*-butylethylene is essentially strainless relative to the saturated hydrocarbon, and we could predict the heat of hydrogenation should be normal, while that for the cis isomer should be some 9.8 kcal above the normal strainless value. With cyclohexene, the alkene is slightly more strained than the alkane, while for the five-membered ring the reverse situation is true, the alkane is slightly more strained. In the latter case the alkene has unfavorable bond angles, and angular strain which is worse than what is found in the alkane, but the torsional energy from eclipsing in the alkane is worse in the alkane than in the alkene, and by a larger amount, so the numbers are as found. The heat of hydrogenation of cyclopentene is thus rather small and similarly for *cis*-cycloheptene. For *cis*-cyclooctene and *cis*-cyclodecene, the same situation prevails qualitatively, but the numbers become increasingly large. This is because the torsional situation and the congestion in the larger ring alkanes become increasingly severe, and the double bond helps to relieve the situation. For the *trans*-cycloalkenes, the situation is quite different. For *trans*-cyclodecene, the alkene, by relieving torsional strain mostly, is less strained than the cycloalkane by 4.1 kcal, and so the heat of hydrogenation would be small. As the ring size of the cycloalkene gets smaller, the torsional strain about the double bond becomes rapidly very severe, so that we see *trans*-cyclooctene has 6.3 kcal of strain more than does the saturated hydrocarbon, while for *trans*-cycloheptene, the number is 19.6 kcal/mol. The remaining numbers in Tables VIII and IX are similarly capable of yielding predictions and/or interpretations of experimental facts.

Conclusions

The force field and minimization scheme described above is capable of supplying structures and energies for a variety of olefins in good agreement with available experimental data. As with any empirical scheme, however, the results can be no more reliable than the accuracy and diversity of the data used to generate the model. For olefins, good structural and thermodynamic information is available only for small acyclic molecules and a very limited number of cyclics; consequently, while all of our calculated data seem qualitatively correct, it is felt to be quantitative only for relatively unstrained systems. It should also be noted that the calculations reported here are not intended to be a compendium of olefin structures, but rather an example, verified where possible, of the utility of the method.

One of the strong points of the program is its ability to study in detail the conformational mobility of a given molecule with particular emphasis on π-bond deformations. This was done, to some extent, for cycloheptene with the implication that most any other system could be similarly studied. An important restriction, however, is that while the program will successfully locate minima on the potential energy surface, saddle points, corresponding to transition states between stable conformations are located only by restricting certain degrees of freedom, r, for the molecule such that the n dimensional saddle point becomes an $(n - r)$ dimensional potential well. Since these restrictions are based on an examination of models along with a certain amount of intuition, our calculated activation enthalpies are subject to a somewhat greater error than is associated with other calculations. The method is also well suited to studies of double bond hybridization and stability as a function of geometrical or steric constraints, such as the trends found in the medium ring *trans*-cyclenes. Such information may be useful in quantitatively explaining and predicting olefin reactivity.

A Test For "Intimacy" in Organic Ion-Pair Transition States by Evaluation of Solvent Electrostriction

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Abstract: Volumes of activation have been determined separately for solvolysis and ion-pair return with rearrangement in benzhydryl thiocyanate and *trans*-α-phenyl-γ-methyallyl *p*-nitrobenzoate. The difference indicates that electrostriction of solvent is only 1–4 ml greater for the solvolytic transition states than for the rearrangement transition states. Both sets of ion-pair transition states cause nearly as much contraction as ordinary ionization reactions for which values of 20–40 ml are commonly observed. The sensitivity of solvent electrostriction to charge separation has been demonstrated by comparison of the partial molar volumes of isomeric hydroxytrimethylanilinium hydroxide inner salts to those of some uncharged structural isomers.

Twenty years ago Winstein and his coworkers[1] reported the first of a long series of studies of solvolytic reactions in which by-products which are isomers of the starting material arise presumably by return from a partially ionized state which has been called the "intimate" ion pair. The kinds of isomerization now

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[1] W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 73, 1958 (1951).

thought to arise in this way include allylic rearrangement of the carbonium-ion component,[1,2] racemization,[3] equilibration of ether and carbonyl oxygen in carboxylate esters,[2] conversion of thiocyanates to isothiocyanates,[4] thionobenzoates to thiolbenzoates,[5] and sulfinates to sulfones.[6] The chief evidence for the intermediacy of intimate ion pairs is that addition of a common ion has been observed not to affect the rate of isomerization although it does affect the rate of exchange and solvolysis.[3,4] Swain,[7] however, has reported that the highly nucleophilic azide ion does suppress the O equilibration of trityl benzoate-*carbonyl*-^{18}O by capturing the intermediate ion pair, and thus preventing its return.

The problem in characterizing the intimate ion pair is to find some measurable property which is sufficiently different from that of starting material or dissociated ions and for which there exists an adequate theory relating the property to the ionization. Such a property is the partial molar volume which can decrease by as much as 50 ml/mol when a substance ionizes.[8] Measurement of the change in volume can be performed either on a transition state or an equilibrium system by determining the effect of pressure on the rate constant or equilibrium constant. Neither the charge separation nor the dipole length of an ion pair is susceptible to experimentally controlled continuous variation, but there is a recent report[9] that the ionization of lithium and sodium fluorenyls in tetrahydrofuran from an initial *tight* ion-pair state to a *loose* one has $\Delta V = -15.6$ and -24.4 ml/mol, respectively. We have sought to supplement this information by measuring the partial molar volumes of some isomeric zwitterions with various distances between the electric poles.

Results and Discussion

The activation volumes for rearrangement and solvolysis of benzhydryl thiocyanate and *trans*-α-phenyl-γ-methallyl *p*-nitrobenzoate are shown in Table I along with the solvolytic activation volumes for several other benzhydryl substrates. The change of volume is negative in accordance with the invariable rule for ionization reactions. This phenomenon, called "electrostriction," is ascribed to the compression of solvent by the attractive force between the charge of the ion and the permanent or induced electric dipoles in the surrounding molecules. It is susceptible to a quantitative theoretical treatment.[8]

The activation volume for $S_{\mathrm{N}}1$ reactions of neutral substrates as well as the volume change for simple ionic equilibrium reactions is the algebraic sum of two terms arising from bond breakage and electrostriction with the latter always dominant. Representative values[10] are, respectively, +10 and −30 ml/mol, so that the net value is −20 ml/mol. It should be noted in passing that the bond-breaking term disappears by cancellation in proton-transfer reactions, and their volume changes can be more negative. The magnitude of the electrostrictive term can be considerably reduced by delocalization of ionic charge,[11] and such an effect might be anticipated for the reactions reported here since the carbonium ions are resonance stabilized.

Table I. Volumes of Activation for Rearrangement (R) and Solvolysis (S)

Substrate	Solvent	T, °C	ΔV, ml/mol
trans-α-Phenyl-γ-methallyl *p*-nitrobenzoate	Me_2CO, 75% HOH, 25%	26.4 26.4	−14 (S) −13 (R)
Ph_2SHSCN	Me_2CO, 95% HOH, 5%	24.0 24.0	−16 (S) −12 (R)
Ph_2CHSCN	Tetrahydrofuran	113.5	−22[a] (R)
Ph_2CHSCN	Benzene	116.0	−21[a] (R)
Ph_2CHSCN	MeCOEt	73.0	−18 (R)
Ph_2CHCl	Me_2CO, 95% HOH, 5%	48.0	−16[b] (S)
$Ph_2CHOCOCH_3$	Me_2CO, 75% HOH, 25%	96.2	−18 (S)

[a] Rate constants for these solvents show an unexpected scatter, and ΔV^* may have an uncertainty of 4 ml. Other values are reliable to 1 ml. [b] A value of −14 ml has been reported for 90% dioxane: D. Buttner and H. Heydtmann, *Ber. Bunsenges. Phys. Chem.*, **73**, 640 (1969).

It is a plausible *a priori* that the volume should decrease monotonically as the substrate ionizes first to the "intimate" state and then to the dissociated or solvent-separated stage. The results of Table I show that the activation volumes for solvolysis and rearrangement (presumably *via* return from the intimate ion pair) have the expected relationship, but the difference is surprisingly small. We conclude that other physical differences between the transition states are also small. The electrostriction phenomenon appears to be well developed in each, and the ionization process must be nearly complete. The competition between solvolysis and external return with exchange at a constant total rate[4] reinforces the idea that ionization in the solvolytic transition state is essentially complete.

In order to draw a strong inference concerning the degree of ionization in intimate ion pairs, we need information about the volumes of well-characterized and variously ionized model systems. For the lower limit we can choose several molecules having coordinate covalent bonds as evidenced by dipole moments in the range 4–5 D. Examples are nitro compounds, amine oxides, and sulfoxides. In these substances the charges are highly developed, but the internuclear distance is only 1.3–1.5 Å. It has been found that the partial molar volumes of these substances are not sensitive to solvent polarity in contrast to the behavior of zwitterions and electrolytes.[12] The molar volumes of the neat liquids are also not greatly different from those of isomers for which polarized structures need not be written; *e.g.*, 2-mercaptoethanol and DMSO have the same volume within 1 ml. We may infer that if the intimate ion pair were fully charged but not separated more than 1.5 Å, the electrostriction effect would have been very small.

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(10) An extensive compilation of measurements is given by W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967).

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(12) K. R. Brower, *ibid.*, **85**, 1401 (1963).

A model for intermediate degrees of ionization can be found in zwitterions in which the dipole length can be varied by positional isomerism. For this purpose we have prepared the *o*-, *m*-, and *p*-hydroxy-*N*,*N*,*N*-trimethylanilinium hydroxide inner salts and measured their partial molar volumes at infinite dilution in water and methanol. The results are shown in Table II.

Table II. Partial Molar Volumes at Infinite Dilution of Hydroxy-*N*,*N*,*N*-trimethylanilinium Hydroxide Inner Salts at 25°

Isomer	Dipole length, Å	Solvent	V_2^0, ml/mol
Ortho	2.85	Water	129
Ortho	2.85	Methanol	114
Meta	4.27	Water	123
Meta	4.27	Methanol	105
Para	5.70	Water	120
Para	5.70	Methanol	(85)

The strong solvent dependence is characteristic of the electrostriction effect, and this is thought to be a consequence of the higher compressibilities of the less polar solvents. It can also be seen that the magnitude of the electrostriction effect increases as the distance between charge centers increases. The molar volumes of all uncharged liquid structural isomers of $C_9H_{13}NO$ which could be found in the chemical handbooks range from 140 to 150 ml, and the volume of the dimethylaminoanisoles is estimated to be 145 ml by applying homologous increments of 16 ml per methylene to the volume of the anisidines, 113 ml. We can construct a crude scale of electrostriction volume *vs.* dipole length as shown in Figure 1. The electrostriction of the zwitterions is taken as 145 ml − V_2^0. A point representing zero electrostriction for the coordinate covalent compounds is included, and the electrostrictions of common uniunivalent electrolytes in water (25 ml) and methanol (50 ml) provide a basis for the expected asymptotic limits shown as horizontal lines in Figure 1.

Since Figure 1 embodies some drastic simplifying assumptions we do not claim a high degree of accuracy for the *x* intercept or the slopes. Nevertheless it shows that electrostriction develops smoothly over a range of several ångströms, and it provides a semiquantitative basis for asserting that the 1–4 ml difference in volume between intimate ion-pair transition states and solvolytic transitions states is almost negligibly small.

Experimental Section

Preparation and Reaction of Benzhydryl Thiocyanate. Benzhydryl bromide was treated with KSCN in acetone according to a general procedure for substituted benzhydryl thiocyanates.[13] A 70% yield was obtained, mp 35–36°. Analyses were first performed by ir absorption,[13] but the precision and accuracy were better with the method of piperidine titration.[4] The extent of solvolysis in reaction mixtures with aqueous acetone as solvent was determined by titration with silver nitrate solution with ferric nitrate as indicator. Both anayses were performed on one sample by partition between water and benzene. The water layer was analyzed for thiocyanate ion, and the benzene layer was analyzed for benzhydryl isothiocyanate.

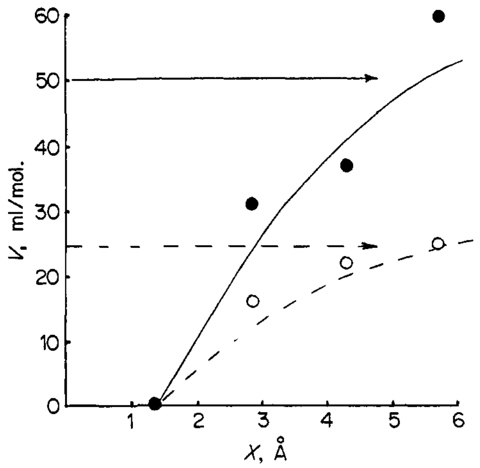

Figure 1. Electrostriction volume *vs.* dipole length for water (○) and methanol (●).

Preparation and Reaction of Benzhydryl Chloride and Benzhydryl Acetate. The chloride and acetate were prepared by treating benzhydrol with thionyl chloride and acetic anhydride, respectively. The products were isolated and purified by distillation. Reaction mixtures were analyzed by titration of the liberated acid.

Preparation and Reaction of *trans*-α-Phenyl-γ-methallyl *p*-Nitrobenzoate. The compound was obtained by the method of Sneen.[14] Reaction mixtures were analyzed by titration of the liberated *p*-nitrobenzoic acid. Analysis for the rearrangement product, *trans*-α-methyl-γ-phenyl *p*-nitrobenzoate, is conveniently based on the fact that it solvolyses much more slowly than the starting material.[2] After ten half-lives of the starting material in 75% aqueous acetone at 24.6°, we found 60% of the theoretical acid at 1200 atm and 59% at ordinary pressure.

High-Pressure Apparatus. The apparatus has been described previously,[15] but the oil-filled thermostat bath has been replaced by a 200-lb aluminum ingot which has been bored to receive the high-pressure vessel. An oil film is used to improve the thermal contact.

Calculation of Activation Volumes. The logarithm of the ratio of the rate constant at pressure to the rate constant at 1 atm (k_p/k_1) was plotted against pressure, and the best straight line was drawn through the origin and other points. The slope was used to evaluate the activation volume according to the equation

$$RT(\partial \ln k/\partial P)_T = -\Delta V^*$$

Preparation of *o*-, *m*-, and *p*-Hydroxy-*N*,*N*,*N*-trimethylanilinium Hydroxide Inner Salts. A solution of 18.2 g (0.17 mol) of *p*-aminophenol in 60 ml of methanol was methylated by addition of 35 ml of methyl iodide in 3 equal portions at 1-hr intervals together with 14 g (0.33 mol) of sodium hydroxide which was added in smaller portions. Crystals of *p*-hydroxy-*N*,*N*,*N*-trimethylanilinium iodide separated and were washed with acetone. The yield was 26 g (56%). A titration curve for an aqueous solution yielded the following results: pK_a = 7.8, equiv wt = 280 (calcd 279). The iodide was causticized with silver oxide suspended in water until iodide ion could no longer be detected in the aqueous phase. The resulting solution was filtered and used for determination of partial molar volume as described below. The concentration was determined by titration with standard acid.

In order to obtain methanolic solutions, the aqueous solution was evaporated to dryness under vacuum, and the residue was dissolved in methanol.

o- and *m*-Aminophenol were subjected to analogous procedures, and equally satisfactory neutralization equivalents were obtained for the methiodides. The values of pK_a were respectively 7.6 and 7.8.

Measurement of Partial Molar Volume at Infinite Dilution. The pycnometer and technique have been previously described.[12] Densities were determined on the most concentrated solutions and progressively diluted solutions in the range from 1.0 to 0.15 *M*. The apparent molar volume was plotted against $c^{1/2}$ and extrapolated to zero concentration.

Acknowledgment. The author is indebted to the National Science Foundation for the support of this work.

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