π diradical, the electronic structure involves degenerate molecular orbitals with opposite stereochemical preference. Thus the concerted and nonconcerted modes of reaction are thought to be equally favorable.[3]

In order to determine the amount of π-diradical character for the open form of these three-membered rings, the lowest energy molecular orbital wave function has been determined for the quasi-planar open forms[4] of each system using the self-consistent-field method with the orbitals approximated as linear combinations of Gaussian orbitals.[5] This wave function may be written, in abbreviated form, as

$$\varphi_1 = \pi_-^{\,2}$$

For these systems there is a second electronic configuration

$$\varphi_2 = \pi_+^{\,2}$$

which is nearly degenerate with the lowest electronic configuration, φ_1. Here, π_+ signifies that the pπ atomic orbitals on the terminal atoms both enter the molecular orbital with a positive coefficient and π_- indicates that these atomic orbitals enter the molecular orbital with coefficients of opposite sign.

The coefficients of φ_1 and φ_2 have been determined for each of the molecules mentioned above using the configuration-interaction method.[1] Once these coefficients are known it is straightforward to determine the amount of π-diradical character, since the wave function for the π diradical

$$\varphi_D = (1/\sqrt{2})(\pi_+^{\,2} - \pi_-^{\,2})$$

to a first approximation is just a linear combination of these two electronic configurations with equal weight and opposite sign.[6] Table I contains the predicted amount of π-diradical character for the open form of several three-membered rings. The main point to be derived from this table is that among these species there are large differences in the amount of π-diradical character. (Since more diradical character means a smaller fraction of the electronic wave function has a stereochemical preference, one should expect appreciable variations in the degree of stereoselectivity in the reaction of these species.) At present the experimental evidence to test this prediction is rather limited; however, it has been reported that the 2 + 3 addition of tetracyanoethylene oxide to olefins[7] and the similar cycloadditions of the aziridines[8] are highly stereoselective (approximately 100%), whereas the pyrolysis of pyrazolines is only moderately stereoselective (30–40%).[9] Assuming each of these reactions proceeds *via* a 0,0 intermediate, this difference can be interpreted conveniently by considering the predicted amount of π-diradical character for each of the ring-open forms.

Table I. π-Diradical Character of the Open Forms of Several Three-Membered Rings[a,b]

Molecule	Calcd weight, % $\pi_+^{\,2}$	Calcd weight, % $\pi_-^{\,2}$	Diradical character,[c] %
Cyclopropane	40	60	80
Cyclopropyl anion	4	96	8
Aziridine	15	85	30
Ethylene oxide	19	81	38
Oxazirane	10	90	20
Ozone	15	85	30

[a] The open forms of these ring systems are CH_2–CH_2–CH_2, CH_2–CH–CH_2, CH_2–NH–CH_2, CH_2–O–CH_2, CH_2–NH–O, and O–O–O. [b] Calculations were carried out for each molecule in the quasi-planar open forms of each ring system for a bond angle of 120°, except for oxazirane, where the bond angle was 126°. The details of these calculations will be reported in a subsequent paper. [c] Note that the diradical wave function $\varphi_D = (1/\sqrt{2})[\pi_+^{\,2} - \pi_-^{\,2}]$ is not orthogonal to $\pi_-^{\,2}$. This presents a problem in interpreting just what one means by the per cent of diradical character. Here we have taken it to be the per cent of the electron density which can be represented by the square of φ_D.

In comparing reaction paths for these species, one needs to consider the stability of the 0,0 open form compared to other geometrical forms. In this connection it should be noted that there seems to be a relationship between the per cent of diradical character and the stability of the open form; *i.e.*, the smaller the diradical character the greater the stability of the 0,0 open form. This may be particularly important in the case of the open forms of cyclopropane, since the amount of diradical character is about 80%. In fact, the recent experiments of Condit and Bergman suggest that the pyrolysis of 2-methyl-3,4-diazabicyclo[3.3.0]oct-3-ene may not involve the 0,0 open form of cyclopropane.[10]

It is hoped that these predictions of the per cent of diradical character of the open forms of three-membered ring systems will stimulate further experimental and theoretical work into the nature of the stereoselectivity of reactions involving the open forms of these systems.

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(3) L. Salem, *Chem. Commun.*, 981 (1970).

(4) The term "quasi-planar open forms" refers to the orientation of the terminal methylene groups, so that the hydrogens lie in the plane of the ring atoms; see ref 5 for further details.

(5) A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *J. Amer. Chem. Soc.*, **92**, 7249 (1970), contains details of the calculations for trimethylene. Similar calculations were carried out for each species mentioned in Table I.

(6) Here it has been assumed that there is no significant amount of charge transfer from one terminal atom to the other.

(7) W. J. Linn, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965).

(8) See, for instance, R. Huisgen, W. Scheer, and H. Huber, *ibid.*, **89**, 1753 (1967), and references therein.

(9) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965).

(10) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971).

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An Experimental Method for Estimating Substituent Effects on Transition-State Structure

Sir:

The success of the transition-state theory of reaction rates has led to frequent discussions of the *structure* of transition states. This has in turn led to a number of speculations and calculations concerning ways of estimating changes in transition-state structure in a series of related reactions, of which Hammond's postulate is perhaps the best known.[1] The problem would be susceptible to an experimental solution if one could find some *measurable* property of a transition state which could then be compared to the same property in the reactants and the products. Our own work dealing with the measurement of enthalpies of transfer of transition states from one solvent to another has suggested such an experimental measure of transition-state structure.[2] The changes in geometry and electron distribution in a set of atoms as they progress along a reaction coordinate might be expected to influence their interaction with a solvent in some continuous way. If two solvents are chosen which are sufficiently different from one another, then the changes in the *difference* in their interaction with the species along the reaction coordinate might reasonably be expected to be a measure of the progress of such species along the reaction coordinate. Thus for a reaction having a substantial solvent effect on its $\Delta H^{\ddagger}$, the degree of resemblance between the transition state and the reactants (or products) should be a function of the similarity between the enthalpy of transfer from one solvent to another of the transition state, δH^{t}, and the enthalpy of transfer from one solvent to the other of the reactants (or products), $\delta\Delta H_{s}$.[3] In particular, as some structural variable in the reaction system is changed one should be able to observe whether the δH^{t} value moves closer to the $\delta\Delta H_{s}$ value of the reactants or of the products, and thus whether that particular variable moves the transition state to the left or to the right along the reaction coordinate. A quantitative scale for substituents could be obtained with respect to this particular property and compared to other measures of substituent properties such as σ values.

I wish to report a preliminary study of this type for the SN2 reaction. The variables examined are: nucleophile, leaving group, and electron-withdrawing and electron-donating substituents on the central carbon atom. A comparison is also made between the two most common charge types of the SN2 reaction: negative nucleophile plus neutral electrophile and neutral nucleophile plus neutral electrophile. A polar protic and a dipolar aprotic solvent are used since they give large differences in enthalpies of activation for SN2 reactions.

Table I. Heats of Solution in Methanol and Dimethylformamide at 25.0°

Compound	ΔH_s (CH_3OH),[a] kcal/mol	ΔH_s (DMF),[a] kcal/mol
NaI	−7.34	−14.42
CH_3SCN	−1.14	−0.41
2,4-Dinitroanisole	6.16	3.15
4-Nitroanisole	5.90	3.79
4-Nitrobenzylpyridinium chloride	4.84	2.52
4-Nitrobenzylpyridinium bromide	7.61	2.18
Benzylpyridinium bromide	5.94	1.53
4-Methylbenzylpyridinium bromide	7.00	2.68

[a] Average of four or more runs, standard deviation 0.10 kcal/mol or better.

Table II. Enthalpies of Transfer of Reactants ($\delta\Delta H_{s}^{r}$), Transition States (δH^{t}), and Products ($\delta\Delta H_{s}^{p}$) of SN2 Reactions from Methanol to Dimethylformamide

Reaction	$\delta\Delta H_{s}^{r}$	δH^{t}	$\delta\Delta H_{s}^{p}$	$\delta H^{t}/(\delta\Delta H_{s}^{p} - \delta\Delta H_{s}^{r})$
$SCN^- + CH_3I$	−4.00[a]	−8.3[a]	−7.38[a]	+2.5
2,4-Dinitrophenoxide + CH_3I	−0.69[a]	−7.1[a]	−8.84[a]	+0.87
4-Nitrophenoxide + CH_3I	3.59[a]	−4.1[a]	−7.94[a]	+0.36
Pyridine + $4\text{-}NO_2C_6H_4CH_2Cl$	−0.95[b]	−7.8[b]	−2.32	+5.7
Pyridine + $C_6H_5CH_2Cl$	0.03[b]	−5.3[b]	−1.30	+4.0
Pyridine + $4\text{-}CH_3C_6H_4CH_2Cl$	0.00[b]	−3.7[b]	−1.21	+3.1
Pyridine + $4\text{-}NO_2C_6H_4CH_2Br$	−1.45[b]	−4.7[b]	−5.43	+1.2
Pyridine + $C_6H_5CH_2Br$	−0.34[b]	−2.0[b]	−4.41	+0.49
Pyridine + $4\text{-}CH_3C_6H_4CH_2Br$	−0.09[b]	−1.5[b]	−4.32	+0.35

[a] Data from ref 2b. [b] Data from ref 2c.

Enthalpies of transfer of the reactants ($\delta\Delta H_{s}^{r}$) and products ($\delta\Delta H_{s}^{p}$) are the differences between the heats of solutions (ΔH_{s}) of those substances in the two solvents. The enthalpy of transfer of the transition state (δH^{t}) is obtained from the relation $\delta H^{t} = \delta\Delta H_{s}^{r} + \delta\Delta H^{\ddagger}$ where $\delta\Delta H^{\ddagger}$ is the difference between the activation enthalpies of the reaction in the two solvents. Table I shows the results of calorimetric measurements[4] of the heats of solution in methanol and dimethylformamide (DMF) of a number of substances of interest. In Table II a comparison is made between the enthalpies of transfer from methanol to DMF of the reactants ($\delta\Delta H_{s}^{r}$), products ($\delta\Delta H_{s}^{p}$), and transition states (δH^{t}) in nine SN2 reactions. As a measure of the resemblance of the transition state to the reactants and to the products the ratio $\delta H^{t}/(\delta\Delta H_{s}^{p} - \delta\Delta H_{s}^{r})$ was calculated.[5] Using this ratio as a criterion for transition-state structure, the following observations can be made. (1) Increasing the basicity of the nucleophile moves the transition state structure closer to that of the reactants.[6] (2) Increasing the basicity of the leaving group moves the transition state closer to the products.[6] (3) Electron withdrawal on the carbon undergoing substitution moves the transition state closer to the products.[6]

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(1) (a) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955). For some other treatments of this problem see (b) J. E. Leffler, *Science*, 117, 340 (1953); (c) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 84, 817 (1962); (d) E. R. Thornton, *ibid.*, 89, 2915 (1967); (e) J. C. Harris and J. L. Kurz, *ibid.*, 92, 349 (1970).

(2) (a) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginsberg, and P. Steinherz, *Chem. Commun.*, 194 (1968); (b) P. Haberfield L. Clayman, and J. Cooper, *J. Amer. Chem. Soc.*, 91, 787 (1969); (c) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg, *J. Org. Chem.*, in press. (d) Another thermodynamic parameter which has been thoroughly studied, particularly by Parker and coworkers [for an excellent review see A. J. Parker, *Chem. Rev.*, 69, 1 (1969)], is the free energy of transfer of a transition state from one solvent to another.

(3) This refers to a one-step reaction. It applies also to any one step and its transition state in a multistep process. Of course measurement of the $\delta\Delta H_{s}$ values of unstable intermediates might not always be possible.

(4) The heats of solution were measured at concentrations as close as possible to those employed in the rate measurements which were used to determine the $\Delta H^{\ddagger}$ values.

(5) The numerical value of this ratio can be any positive or negative number and no simple relationship exists between its numerical value and the structure of the transition state. Thus, for example, a value of 0.50 does not mean that the structure of the transition state is half-way between that of the reactants and that of the products. The ratio indicates *changes* in transition-state structure as some structural variable in the reaction in question is changed, a shift toward a higher value in the ratio indicating a shift toward products in the transition-state structure.

(6) Conclusions 1 and 2 are predicted by the rule of Swain and Thornton;[1c] conclusions 1, 2, and 3 are predicted by the rules of Harris and Kurz.[1e]

(4) Other factors being equal, in SN2 reactions having a neutral nucleophile and a neutral electrophile the transition state resembles the reactants more than is the case in SN2 reactions having a negative nucleophile and a neutral electrophile.[7]

The ready availability of $\Delta H^{\ddagger}$ values in several solvents for many reactions as well as the ease of measuring the heats of solution of the reactants and of the products in most cases makes this a promising method for obtaining an *experimental* measure of the effects of structural and other variables upon the structures of transition states.

(7) The suggestion that there is little charge separation in the transition state of the Menshutkin reaction was made recently by M. H. Abraham, *Chem. Commun.*, 1307 (1969).

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Halide–Halide Exchange at Asymmetric Silicon. New Evidence against a Siliconium Ion-Pair Mechanism

Sir:

In 1964 we published a preliminary report[1] containing data which seemed quite consistent with the proposal of a siliconium ion-pair mechanism for the chloride–radiochloride exchange of optically active α-NpPhMeSi*Cl (I) with $c\text{-}C_6H_{11}NH_3{}^{36}Cl$ in chloroform solvent. Despite the rather formidable array of evidence presented in our earlier report, we have now assembled completely convincing evidence that the siliconium ion-pair mechanism originally proposed for this reaction is incorrect.

We wish to communicate our new results because of their mechanistic importance. At present, the data in ref 1 favoring a siliconium ion-pair mechanism comprise, according to a recent reference,[2] "... the only well documented evidence for this mechanism in organosilicon chemistry ...."

Several lines of new evidence are summarized below.

Modern instrumentation unavailable to us in our previous studies was used for careful redetermination of the k_{rac}/k_{ex} ratio for α-NpPhMeSi*Cl (I). Radioactivity counting was done using a Packard Model 3002 Tri-carb liquid scintillation spectrometer. Racemization was followed using a Durrum-Jasco automatic digital polarimeter series J-180, accurate to ±0.002. Instead of our previous value of 1.0 ± 0.1 for the ratio, we now find $k_{rac}/k_{ex} = 1.3 \pm 0.1$. This ratio is independent of any assumptions concerning the order of the exchange or racemization reactions in salt. The k's are first-order rate constants;[3] conditions and concentrations of reactants (chlorosilane and salt both at 0.089 M in chloroform at 25.5°) were identical for racemization and exchange studies. In addition, using the same conditions and concentrations of reactants in chloroform solvent, we have now determined the k_{rac}/k_{ex} ratios for two other optically active systems. For the new optically active chlorosilane,[4] $\alpha\text{-NpPh}_F\text{MeSi*Cl}$ (II), the perfluorophenyl analog of α-NpPhMeSi*Cl, $k_{rac}/k_{ex} = 2.0 \pm 0.1$. For the optically active chlorosilane,[5] $Ph_3SiSi^*(Ph)(Me)Cl$ (III), $k_{rac}/k_{ex} = 1.8 \pm 0.1$. Of itself, variation in the k_{rac}/k_{ex} ratio from 1.3 to 2.0 to 1.8 for I, II, and III, respectively, leads only to the conclusion that in the case of II each act of exchange proceeds with inversion, and that the ratios of 1.8 and 1.3 represent increasing importance of retention or racemization mechanisms for exchange reactions of III and I. However, comparing rate constants for exchange and racemization for chlorosilanes II and I gives the results: $k_{ex}(II)/k_{ex}(I) = 1.1$ and $k_{rac}(II)/k_{rac}(I) = 1.7$. Thus, replacement of a phenyl group in I by a perfluorophenyl group gives II and also gives somewhat *increased* rates of exchange and racemization. This is in direct conflict with a siliconium ion-pair mechanism. Operation of the latter should give greatly *decreased* rates for II because of its strongly electron-withdrawing perfluorophenyl substituent. Thus, these data point to a mixture of inversion and retention mechanisms for halide–halide exchange of I in chloroform.

The above conclusion, that the polar effects of substituents on the rate of chloride–chloride exchange of chlorosilanes, under the conditions defined above, is not in accord with a siliconium ion-pair mechanism, was reinforced by a study of the rates of chloride–chloride exchange for a series of optically inactive chlorosilanes. These had the general structure α-Np-Me(Aryl)SiCl in which aryl comprised meta- and para-substituted phenyl groups suitable for a Hammett type σ–ρ study. Using phenyl substituents such as m-CF$_3$, p-CF$_3$, p-OCH$_3$, and p-CH$_3$, ρ was found to be very small and positive ($\rho = 0.4 \pm 0.1$). Since ρ for a siliconium ion-pair mechanism would be expected to be large and negative (SN1 solvolyses have $\rho = \sim -3$ for tertiary organic halides), this study provides strong evidence against such a mechanism. Indeed it indicates very little change in charge for transition-state silicon compared to ground-state silicon in these halide–halide exchanges. Evidently, bond making and bond breaking have taken place to approximately equal extents in the rate-controlling transition states of these reactions.

Previously, we concluded from infrared studies of equilibrium 1 that an equimolar mixture of R_3Si^*Br

$$R_3Si^*Br + c\text{-}C_6H_{11}NH_3Cl \rightleftarrows R_3Si^*Cl + c\text{-}C_6H_{11}NH_3Br \quad (1)$$

and $c\text{-}C_6H_{11}NH_3Cl$ produced an equilibrium system containing less than 2% of the original R_3Si^*Br. Using radiochloride salt we have now found that the equilibrium concentration of R_3Si^*Br actually amounts to 9.9%. This revision of the equilibrium constant for eq 1 renders invalid one of the key links in the prior chain of evidence implicating a siliconium ion-pair mechanism. The incorrect earlier data led to the

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(1) L. H. Sommer, F. O. Stark, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 5683 (1964); see also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, pp 98–100.

(2) M. W. Grant and R. H. Prince, *Chem. Commun.*, 1076 (1968).

(3) For racemization, k_{rac} is simply the pseudo-first-order rate constant; for exchange k_{ex} is the first-order rate contant defined by $k_1 = R/a$ in which R is the gross rate of exchange and a is the concentration of chlorosilane; for detailed treatment, see: (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 192–193; (b) M. W. Grant and R. H. Prince, *J. Chem. Soc. A*, 1138 (1969).

(4) Unpublished work of L. H. Sommer and M. A. Silverman; see M. A. Silverman, Ph.D. Thesis, University of California at Davis, 1970.

(5) L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, **91**, 7067 (1969).