On the Mechanism of Proton Transfer in Solution. Factors Determining Whether the Activated Complex Has an Equilibrated Environment

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Abstract: A proton-transfer event in solution requires repolarization of the surrounding solvent. Since the time required for translation of the proton should be short in comparison to the reorientational relaxation time of the solvent, such fast protonic motions are resisted by a force (with force constant, F_{sr}) which would not be present if solvent relaxation were fast. It is shown that the mechanism of proton transfer depends on the magnitude of F_{sr}; three distinct possible mechanisms are predicted. Evaluation of F_{sr} using an electrostatic model based on a cylindrical cavity in a continuous dielectric medium leads to the following conclusions. (1) Proton transfers involving small bases (*e.g.*, H_2O) should commonly follow a coupled mechanism in which the proton rides across between the bases in a potential well which results from the solvent-derived restoring force; translation along the reaction coordinate corresponds to motion of this well and not to free translation of the proton. (2) Proton transfers between large bases should occur *via* a three-step process: first solvent reorganizes into the configuration which is appropriate for the transition state, then the proton transfers, and finally solvent relaxes into the product configuration. (3) A second three-step mechanism in which the solvent configuration is not in equilibrium with the internal structure of the activated complex is possible for transfers between bases of intermediate size but should be very rare. Predictions are compared to experimental data and this theory is shown to provide a unified explanation for many observations (of $\Delta S^{\ddagger}$, isotope effects, etc.) which were previously thought to be anomalous.

The rates and mechanisms of many proton-transfer reactions in solution have received intensive study. However, many aspects such as the observed kinetic isotope effects and thermodynamic activation parameters are incompletely understood.

Any general mechanism for such transfers must cope with the fact that a proton-transfer event is accompanied by a change in the internal charge distribution of the reactants. Several workers[1-3] have pointed out that this shift in internal charge distribution is expected to occur within a time period which is up to 1000 times as short as that required for repolarization of the surrounding medium. In its simplest form, such an argument contrasts the macroscopic dielectric relaxation times observed for common solvents (10^{-10}–10^{-12} sec) with the expected natural duration of a successful proton-transfer event (*ca.* 10^{-13} sec). Such time estimates have previously often been assumed to imply that the polarization of the solvent in the neighborhood of the activated complex is not in equilibrium with the internal charge distribution.

Nearly all current mechanistic interpretations of reactions in solution assume implicitly that the activated complex may be treated as if all available states have their equilibrium populations. Any proof of the common existence of nonequilibrium solvation would therefore have serious general implications. However, many of the observations which can be attributed to nonequilibrium solvation can also be interpreted in terms of mechanisms which explicitly assume fully equilibrated transition states.[4,5] In a related example drawn from outside the field of proton-transfer reactions, anomalous solvent effects which might seem to imply nonequilibrium solvation have been successfully qualitatively rationalized by Ritchie, Skinner, and Badding[6] in terms of a mechanism which both "requires. . .solvent reorientation as an essential part of the activation process" and assumes the solvent to be in equilibrium with the internal charge distribution in the transition state.

In this paper, a quantitative model for proton-transfer processes is described. A general argument which defines the possible mechanisms and formulates the criteria which determine which of those mechanisms is followed is presented first. A simple electrostatic cavity model is then used to estimate the magnitudes of the parameters which appear in those general criteria. Finally, predictions based on the model are compared to the available experimental data. It is shown that reactions in which the activated complex has a nonequilibrated environment should be rare, and that, when they do occur, the deviation of solvent configuration from its equilibrium state is expected to be toward that configuration which is appropriate for an internal structure in which the proton is *half* transferred. This quantitative model and some of its predictions are shown to be related both to qualitative suggestions made earlier by Schowen[7] and by Ritchie,[5,6] and to Marcus' theoretical treatments of weak-overlap electron-transfer reactions[8] and proton-transfer reactions.[9,10]

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[1] (a) E. Grunwald and E. Price, *J. Amer. Chem. Soc.*, **86**, 2970 (1964); (b) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965).

[2] (a) M. M. Kreevoy and R. A. Kretchmer, *J. Amer. Chem. Soc.*, **86**, 2435 (1964); (b) M. M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 63 (1968).

[3] R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1965).

[4] A. J. Kresge, Y. Chiang, and Y. Sato, *J. Amer. Chem. Soc.*, **89**, 4418 (1967).

[5] C. D. Ritchie, *ibid.*, **91**, 6749 (1969).

[6] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

[7] (a) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *ibid.*, **87**, 1553 (1965); (b) L. D. Kershner and R. L. Schowen, *ibid.*, **93**, 2014 (1971).

[8] (a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); (b) *Discuss. Faraday Soc.*, **29**, 21 (1960); (c) *J. Phys. Chem.*, **67**, 853 (1963); (d) *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (e) *J. Chem. Phys.*, **43**, 679 (1965).

[9] (a) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); (b) A. O. Cohen and R. A. Marcus, *ibid.*, **72**, 4249 (1968).

A General Argument

Consider the transfer of a charge from one site in a solution to a second site; let that transfer be so rapid that the polarization of the medium remains unchanged. If that polarization is in equilibrium with the charge at the first site, then work must be done to effect the transfer, and that work will be equal to the accompanying increase, ΔU, in the internal energy of the system (since fixed polarization implies $\Delta S = \Delta V = 0$).

This general conclusion may be applied to the specific case of proton-transfer reactions. Such reactions are commonly formulated as occurring in three steps.[11]

$$\mathrm{BH^+ + B'} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{BH^+\cdots B'} \quad (1)$$

$$\mathrm{BH^+\cdots B'} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{B\cdots HB'^+} \quad (2)$$

$$\mathrm{B\cdots HB'^+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{B + B'H^+} \quad (3)$$

where eq 1 and 3 represent encounter of the reactants and separation of the products. The caged acid–base pairs, $\mathrm{BH^+\cdots B'}$ and $\mathrm{B\cdots HB'^+}$, are here written as if hydrogen bonded, even though such interactions would be very weak for acids such as nitroalkanes,[5] in order to emphasize that this discussion is concerned with the proton-transfer step (eq 2) *per se* as it occurs between two suitably positioned and oriented bases.[12]

Since solvent reorganization should be slow in comparison to vibrational displacements of the proton, all such displacements which are accompanied by a changing internal charge distribution must lead to an increase in the internal energy, U, of the solvated BHB′ system. For motion on a vibrationally fast time scale, the proton is thus confined in a potential well which arises from its interaction with the solvent. In particular, the antisymmetric stretching vibration of the activated complex

$$(\overleftarrow{\mathrm{B}}\cdots\overrightarrow{\mathrm{H}}\cdots\overleftarrow{\mathrm{B}}')^{+\ddagger}$$

which is commonly identified with the reaction coordinate for proton transfer,[13] is accompanied by a large displacement of charge and should be especially subject to such constraint. This constraint of vibration along the reaction coordinate is shown below to lead to the existence of *two distinct types of possible mechanisms* for eq 2. These will be referred to as the "coupled" and "uncoupled" mechanisms, the names indicating respectively that the proton transfer does or does not occur in synchrony with solvent reorganization.

Three Model Processes. In interpretations of the parameters which characterize the possible mechanisms for eq 2, it will be useful to compare them to the corresponding parameters for three model processes. Let the first of these processes be called the "chemical" mechanism and be defined as the mechanism which would be followed if the rate at which the solvent configuration equilibrates with the internal structure were very fast compared with all internal motions. The parameters which characterize this fully coupled and equilibrated hypothetical mechanism will be referred to as the "chemical" contributions to the corresponding parameters for the correct mechanism and will be denoted by a subscript ch.

In the second model process, the internal structure remains fixed while the solvent reorganizes from the configuration which is in equilibrium with that fixed internal structure into a second configuration which would be in equilibrium with some second specified internal structure. The parameters corresponding to such a solvent reorganization process will be denoted by a subscript sr.

In the third process, the solvent configuration remains fixed while BHB′ rearranges from the internal structure which is in equilibrium with that fixed solvent configuration into the second specified internal structure. It will be assumed in the following discussion that the potential energy change, $\Delta U_{0,\mathrm{sr}}$, for the second model process is identical with the contribution from changes in solvent–solute interactions to the value of ΔU_0 for this third process. This assumption is exactly true for the electrostatic model for transfer between uncharged bases which is presented below. Serious deviations from this approximation are expected only when there is a large difference between the two bases, B and B′, either in their steric hindrance to approach by solvent or in their charge; the effects of such deviations are discussed in the section on the electrostatic model.

Uncoupled Mechanisms. If both solvent relaxation and vibrational motions of the proton occur at their natural rates, then the mechanism for proton transfer (eq 2) must be uncoupled; the solvent configuration cannot be in equilibrium with the internal charge distribution at all points along the reaction coordinate. It is possible, however, for the solvent to repolarize prior to the occurrence of the internal process. The mechanism is then a three-step process: solvent reorganization out of the configuration which is in equilibrium with the internal structure of the reactant ($\mathrm{BH^+\cdots B'}$) into some intermediate configuration, followed by the change in internal structure, and then a final relaxation of the solvent into the equilibrium configuration for the products. In such a mechanism, the solvent could be in equilibrium with the internal structure at a maximum of three points along the reaction coordinate: in the initial state, in the final state, and in one intermediate state. A similar three-step process has been shown by Marcus[8] to be the expected mechanism for weak-overlap electron-transfer reactions.

The total potential energy profile, U_0, for fast displacements of the proton along the axis of the BHB′ system (*i.e.*, for uncoupled motion of the BHB′ system along the internally defined reaction coordinate) is a sum of two contributions. One is the chemical barrier, $U_{0,\mathrm{ch}}$, for the first model process defined above; the second is the potential well, $U_{0,\mathrm{sr}}$, produced by the polarization of the solvent and corresponding to the second and third model processes. The minimum in that well lies at that position of the proton for which the solvent polarization is the equilibrium configuration.

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(10) M. M. Kreevoy and D. E. Konasewich, *Advan. Chem. Phys.*, **21**, 243 (1971).

(11) *E.g.*, C. D. Ritchie in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 246.

(12) Also, since the presence of one or more bridging solvent molecules in eq 2 would not change the argument, such bridges are not explicitly included.

(13) *E.g.*, F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

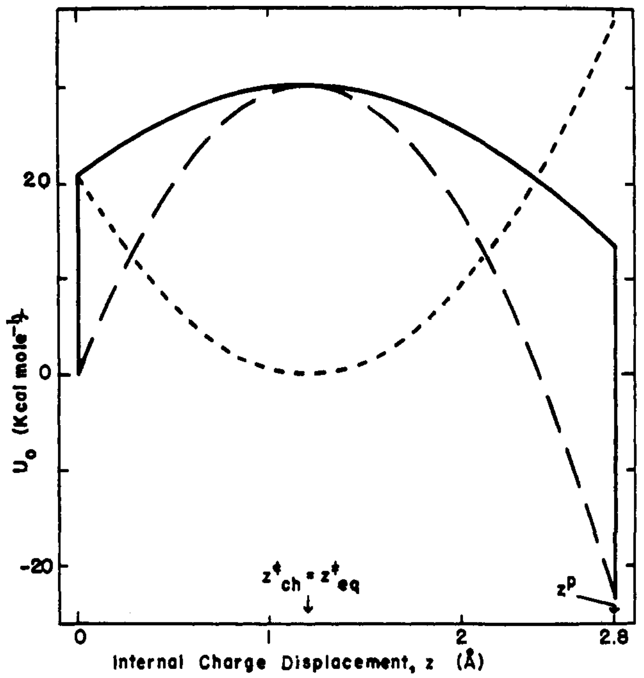

Figure 1. The first uncoupled mechanism, showing construction of the total U_0 as a function of the internal charge displacement, z: (— —) $U_{0,ch}$ (eq 4) with $\Delta U_0{}^{\ddagger}{}_{ch} = 30$ kcal mol^{-1}, $z_{ch}{}^{\ddagger} = 1.2$ Å, $z^p = 2.8$ A, $F_{ch} = -2.90 \times 10^4$ dyn cm^{-1} (eq 20); (-----) $U_{0,sr}$ (eq 5) with $z_{eq}{}^{\ddagger} = z_{ch}{}^{\ddagger}$ (eq 9), $F_{sr} = 2 \times 10^4$ dyn cm^{-1} (eq 19 for transfer from H_3O^+); (———) total U_0 (eq 6) with total $\Delta U_0{}^{\ddagger} = 30$ kcal mol^{-1}; total $\Delta U_0{}^{\circ} = -23.35$ kcal mol^{-1}.

This summation is, of course, exact only in the limit as solvent reorganization becomes very slow compared to displacement of the proton but will be a useful approximation whenever a significant difference exists between the rates of those two processes. If the time required for solvent relaxation became comparable to that for protonic displacement, three-step mechanisms which are in a sense intermediate between the purely coupled and purely uncoupled mechanisms described here would become possible; in such borderline mechanisms, a significant fraction of the total solvent reorganization could occur simultaneously with the second (internal) step. However, it would remain true that complete equilibrium between the solvent polarization and the internal charge distribution could be present at no more than three points along the reaction coordinate.

In order to facilitate visualization of the behavior of the potential energy profile as $U_{0,ch}$ and $U_{0,sr}$ are varied, let it be assumed that both potentials are adequately approximated by parabolas. The chemical barrier is then given by

$$U_{0,ch} = \Delta U_0{}^{\ddagger}{}_{ch} + \frac{1}{2}F_{ch}(z - z^{\ddagger}{}_{ch})^2 \qquad (4)$$

where $\Delta U_0{}^{\ddagger}{}_{ch}$ is the barrier height, F_{ch} is the (negative) force constant for the barrier, and $z^{\ddagger}{}_{ch}$ is the position of the chemical transition state along the z axis; the origin ($U_{0,ch} = 0$, $z = 0$) is located at the reactants (see Figures 1 and 2). Similarly, the solvent well is described by

$$U_{0,sr} = \frac{1}{2}F_{sr}(z - z_{eq})^2 \qquad (5)$$

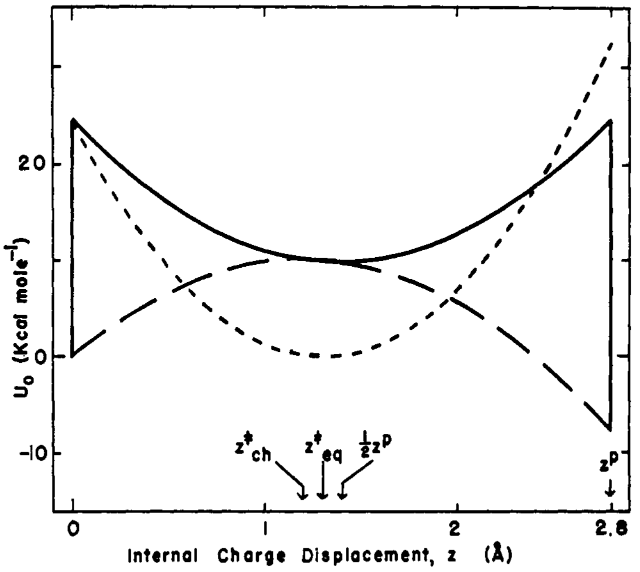

Figure 2. The second uncoupled mechanism, showing construction of the total U_0 as a function of the internal charge displacement, z: (— —) $U_{0,ch}$ (eq 4) with $\Delta U_0{}^{\ddagger}{}_{ch} = 10$ kcal mol^{-1}, $z^{\ddagger}{}_{ch} = 1.2$ Å, $z^p = 2.8$ Å, $F_{ch} = -0.965 \times 10^4$ dyn cm^{-1} (eq 20); (-----) $U_{0,sr}$ (eq 5) with $z^{\ddagger}{}_{eq} = 1.304$ (eq 11), $F_{sr} = 2 \times 10^4$ dyn cm^{-1} (eq 19 for transfer from H_3O^+); (——) total U_0 (eq 6) with total $\Delta U_0{}^{\ddagger} = 24.44$ kcal mol^{-1}, total $\Delta U_0{}^{\circ} = -7.79$ kcal mol^{-1}.

where F_{sr} is the (positive) force constant for vibration of the proton in the solvent well and z_{eq} is the position of the minimum in that well. In conformance with the assumed identity of the values of ΔU_0 for the second and third model processes, F_{sr} is assumed not to vary significantly as z_{eq} varies over the range $z = 0$ (for reactants) to $z = z^p$ (for products).

The total potential, U_0, given by

$$U_0 = U_{0,ch} + U_{0,sr} \qquad (6)$$

is thus a function of both z and z_{eq}. Since the transition state lies at the maximum value of U_0 in the range, $0 \leqslant z \leqslant z^p$, its location, $z^{\ddagger}$, is a function of z_{eq} which can be found by maximizing U_0 with respect to z. The correct value of z_{eq} must then be the one which minimizes that maximum U_0 and thus gives the lowest possible total barrier. The solution to this minimax problem depends on the relative magnitudes of the two force constants; two very different potential energy profiles (and mechanisms) are predicted for the two cases, $F_{sr} < |F_{ch}|$ and $F_{sr} > |F_{ch}|$.

The First Uncoupled Mechanism. If $F_{sr} > |F_{ch}|$, then it follows from eq 4–6 that U_0 has a single extremum along z and that extremum is a maximum (*i.e.*, that extremum is the transition state). The location, $z^{\ddagger}$, of the transition state on the reaction coordinate is given by

$$z^{\ddagger} = \frac{F_{ch}z^{\ddagger}{}_{ch} + F_{sr}z_{eq}}{F_{ch} + F_{sr}} \qquad (7)$$

Minimization of this $U_{0,max}$ with respect to z_{eq} leads to the following algebraic characterization of the transition state.

$$U_0{}^{\ddagger} = \Delta U_0{}^{\ddagger} = \Delta U_0{}^{\ddagger}{}_{ch} \qquad (8)$$

$$z^{\ddagger} = z^{\ddagger}{}_{ch} = z^{\ddagger}{}_{eq} \qquad (9)$$

where $z^{\ddagger}{}_{eq}$ is the position of the minimum in the solvent

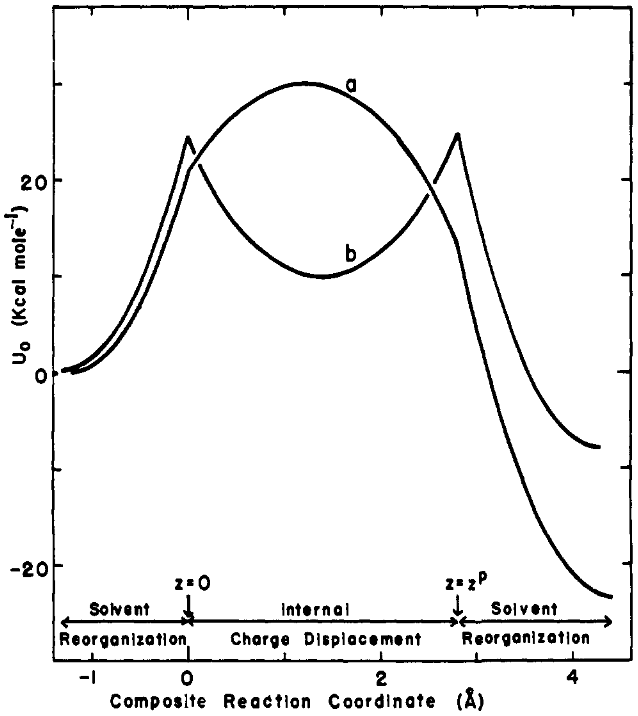

Figure 3. (a) The first uncoupled mechanism, and (b) the second uncoupled mechanism, showing the total U_0 curves as functions of the three-step reaction coordinate. These curves are constructed using the same values of parameters as those listed for Figures 1 and 2.

well when U_0 is at its minimized maximum. For an example of this behavior, see Figures 1 and 3a; the force constants and other parameters used in constructing those figures are chosen in accord with estimates for proton transfer from H_3O^+ calculated in the section describing the electrostatic model.

In verbal summary, if solvent relaxation is slow compared to motion of the proton and if the potential well, $U_{0,\mathrm{sr}}$, for solvent relaxation is less sharply curved than the potential barrier, $U_{0,\mathrm{ch}}$, for the chemical model process, then the activated complex for the actual mechanism will have the *same* internal structure and solvent configuration as it would if solvent reorganization occurred in synchrony with the proton motion. The solvent configuration surrounding the activated complex is thus fully equilibrated with the internal structure and all of the observable activation parameters ($\Delta G^{\ddagger}, \Delta S^{\ddagger}, \Delta V^{\ddagger}, \ldots$)[14] must be identical with those for the hypothetical single-step chemical mechanism. However, even though the rate of the overall proton-transfer process (eq 2) will be operationally indistinguishable from the rate expected for that one-step mechanism, the differing time scales of the internal and solvent motions require that the actual course of the reaction be the three-step uncoupled mechanism in which the solvent configuration anticipates the proton-transfer event.

The Second Uncoupled Mechanism. If $F_{\mathrm{sr}} > |F_{\mathrm{ch}}|$, then the single extremum in U_0 along z can be shown to be a minimum. In the range, $0 \leqslant z \leqslant z^{\mathrm{p}}$, the maximum value of U_0 (*i.e.*, the transition state) must thus lie at either $z = 0$ or $z = z^{\mathrm{p}}$. The minimum possible value of that maximum must therefore correspond to the value of z_{eq} for which

$$U_0(z_{\mathrm{eq}} = z^{\ddagger}_{\mathrm{eq}}, z = 0) = U_0(z_{\mathrm{eq}} = z^{\ddagger}_{\mathrm{eq}}, z = z^{\mathrm{p}}) \quad (10)$$

which leads to

$$z^{\ddagger}_{\mathrm{eq}} = \frac{z^{\mathrm{p}}}{2} + \frac{F_{\mathrm{ch}}}{F_{\mathrm{sr}}}\left(\frac{z^{\mathrm{p}}}{2} + z^{\ddagger}_{\mathrm{ch}}\right) \quad (11)$$

Since the first activated complex lies at $z = 0$, $U_{0,\mathrm{ch}}$ is unchanged during the activation process and from eq 5, 6, and 10

$$\Delta U_0^{\ddagger} = U_{0,\mathrm{sr}}(z_{\mathrm{eq}} = z^{\ddagger}_{\mathrm{eq}}, z = 0) \quad (12)$$

From eq 11, the position of the minimum in the solvent well in the transition state is a function of the force constant ratio; its extreme locations are given by the two limits: as $F_{\mathrm{sr}}/|F_{\mathrm{ch}}| \rightarrow \infty$, $z^{\ddagger}_{\mathrm{eq}} \rightarrow {}^{1}/_{2}z_{\mathrm{p}}$, and as $F_{\mathrm{sr}}/|F_{\mathrm{ch}}| \rightarrow 1$, $z^{\ddagger}_{\mathrm{eq}} \rightarrow z^{\ddagger}_{\mathrm{ch}}$ (*i.e.*, the second and first uncoupled mechanisms become identical at $F_{\mathrm{sr}} = |F_{\mathrm{ch}}|$). An example of this class of behavior is illustrated in Figures 2 and 3b, the parameters of which are identical with those of Figure 1 except that $\Delta U_0{}^{\ddagger}{}_{\mathrm{ch}}$ is 10 instead of 30 kcal mol^{-1}.

In verbal summary, if the solvent well, $U_{0,\mathrm{sr}}$, is more sharply curved than the chemical barrier, $U_{0,\mathrm{ch}}$, and if an uncoupled mechanism is followed, then the proton transfer (eq 2) will take place in three steps, just as in the first uncoupled mechanism. However, there will be *two* transition states of equal total energy: one has an internal structure identical with that of reactant ($BH^+ \cdots B'$); the other has an internal structure identical with that of product ($B \cdots HB'^+$); both have the same solvent structure. That solvent structure is *not* in equilibrium with either activated complex. Except for the statistical factor of 2 which arises from the partitioning of the intermediate at the minimum in U_0, the observed activation parameters[14] will contain *no* contributions from changes in internal structure and will be functions *only* of the change in solvent configuration (the second model process). However, the extent of the change in solvent configuration (and thus indirectly the magnitude of the activation parameters) will depend on the structure of the hypothetical corresponding chemical activated complex. Thus for a symmetric proton transfer between identical bases ($\Delta U_0{}^{\circ} = 0$, $z^{\ddagger}_{\mathrm{ch}} = {}^{1}/_{2}z^{\mathrm{p}}$), eq 11 requires that the solvent have the halfway configuration ($z^{\ddagger}_{\mathrm{eq}} = {}^{1}/_{2}z^{\mathrm{p}}$) and thus be appropriate for the internal structure of the chemical activated complex. For unsymmetric transfers, the solvent configuration is predicted to lie between that halfway arrangement and the configuration appropriate for the now unsymmetric internal structure of the chemical activated complex; it will be more product-like (${}^{1}/_{2}z^{\mathrm{p}} < z^{\ddagger}_{\mathrm{eq}} \leqslant z^{\mathrm{p}}$) for uphill ($\Delta U_0{}^{\circ} > 0$) reactions and more reactant-like ($0 \leqslant z^{\ddagger}_{\mathrm{eq}} < {}^{1}/_{2}z^{\mathrm{p}}$) for downhill ($\Delta U_0{}^{\circ} < 0$) reactions. The extent to which the solvent deviates from the halfway configuration decreases as the curvature of the solvent well increases.[15]

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(14) In this discussion, the standard Gibbs free energy of activation, $\Delta G^{\ddagger}$, is that defined by the Eyring equation [W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, 3, 492 (1935)], $\Delta G^{\ddagger} = -RT \ln K^{\ddagger} = -RT \ln (kh/k_{\mathrm{b}}T)$, where k is the rate constant of the step to which $\Delta G^{\ddagger}$ refers, and the transmission coefficient is implicitly assumed to be unity. Other thermodynamic functions for activation are defined in terms of the usual relationships between those functions and G.

(15) Although the models on which the arguments are based differ in many respects, it is interesting to note how closely these conclusions about the mechanism of proton transfer for the case in which $F_{\mathrm{sr}} \geqslant |F_{\mathrm{ch}}|$ parallel those derived by R. A. Marcus[8] for weak-overlap electron transfers.

The Coupled Mechanism. From the above discussion, it follows that if $F_{\mathrm{sr}} > |F_{\mathrm{ch}}|$, then any further increase in F_{sr} will lead to an increase in $\Delta U_0^{\ddagger}$ (eq 12 and 5). If $\Delta U_0^{\ddagger}$ for the second uncoupled mechanism increases sufficiently, then the rate for that mechanism will be decreased enough to allow a coupled mechanism to compete successfully.

In such a coupled mechanism, the hydrogenic vibration along the reaction coordinate is slowed by coupling it to the rotational fluctuations in solvent structure. The solvent configuration is in equilibrium with the internal structure at all points along the reaction coordinate, as in the chemical model process. However, the rate-determining step is a fluctuation in solvent configuration whose rate constant may be identified with τ^{-1}, the reciprocal of the microscopic dielectric relaxation time (or molecular reorientational correlation time) for the solvent in the neighborhood of the BHB′ complex. In this mechanism, the internal motion and the solvent reorganization may be said to have exchanged the roles which they are commonly thought to play. Instead of protonic displacement (*i.e.*, the antisymmetric stretch of BHB′) defining the reaction coordinate while the solvent merely adjusts its configuration to provide maximum stabilization of the internal structure, motion along the reaction coordinate through the transition state now corresponds to a cooperative reorientation of solvent molecules while the proton adjusts its position accordingly. The proton rides across from a site near B to a site near B′ in the potential well defined by $U_{0,\mathrm{sr}}$ as that well changes the position of its minimum (*i.e.*, as z_{eq} increases). At each point along the reaction coordinate, the potential energy of the system is equal to $U_{0,\mathrm{ch}}$, the proton lies at the minimum in $U_{0,\mathrm{sr}}$, and any vibrational motion of the proton experiences a positive restoring force.

For the proton to be transferred in this manner, the BHB′ system requires sufficient free energy both to allow passage over the chemical barrier and to allow the fluctuation in z_{eq} to take place. The rate will thus be slower than that of the hypothetical chemical mechanism, and the observed rate constant and free energy of activation[14] will be related approximately[16] to the corresponding parameters for the chemical mechanism by

$$k = (h/\tau kT)k_{\mathrm{ch}} \tag{13}$$

$$\Delta G^{\ddagger} = \Delta G_{\mathrm{ch}}^{\ddagger} + RT \ln (\tau kT/h) \tag{14}$$

In its requirement that the proton remain at a potential minimum throughout its transfer, this mechanism is in accord with the Swain, Kuhn, and Schowen mechanism[7a] for proton transfer in acid–base catalysis and with Cordes' modification[17] of that mechanism. It differs, however, in one important respect; at least in Cordes' more explicit formulation, the minimum in which the proton resides is attributed in these earlier proposals entirely to internal force fields; in the mechanism proposed here, the minimum arises from solute–solvent interactions. A close relationship also exists between the mechanism presented here and the qualitative suggestions of Ritchie[5,11] concerning the role of solvent reorganization in proton-transfer reactions.

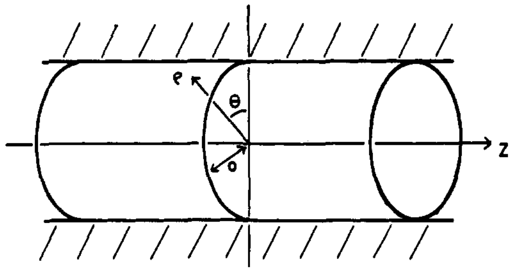

Figure 4. Infinite cylindrical cavity of radius a in a continuous dielectric medium. Cylindrical coordinates (z, ρ, θ) are indicated.

An Electrostatic Model

The general discussion given above has outlined the possible mechanisms for proton transfer and has shown how the magnitude of the solvent-derived restoring force determines which mechanism will be followed. In order to predict observable behavior, it is necessary to be able to estimate approximately how large that restoring force will be and how its magnitude will depend on the choice of solvent and reactants. For most proton-transfer reactions, the dominant contribution is likely to be electrostatic in origin although contributions from such sources as hydrogen bonding and hydrophobic interactions are also possible. The magnitude and functional form of the electrostatic contribution to that restoring force is estimated below from a simple dielectric cavity model.

Transfer between Uncharged Bases. If both bases are uncharged (as in eq 2), then, as discussed above, proton transfer is accompanied by a displacement of the center of gravity of positive charge from a point in or near B to a point in or near B′. If B and B′ are of comparable size, then the BHB′ system can be modeled by a cylindrical cavity of radius a in a continuous medium characterized by a dielectric constant D (Figure 4). The internal dielectric constant of the cavity will be taken as unity. If the center of positive charge in the BHB′ system is represented by a point charge at the origin ($z = 0$, $\rho = 0$), then the equilibrium electrostatic potential will be cylindrically symmetrical and its value at any point within the cavity can be expressed in the form[18]

$$V(z,\rho) = q/(\rho^2 + z^2)^{1/2} + \frac{2q}{\pi}\int_0^{\infty} \frac{(1 - D)kaK_0(ka)K_1(ka)I_0(k\rho)}{1 - (1 - D)kaI_0(ka)K_1(ka)} \cos (kz)\, \mathrm{d}k \tag{15}$$

where K_0, K_1, and I_0 are modified Bessel functions and the electrostatic system of units is employed.

The second term in eq 15 gives the contribution to $V(\rho,z)$ which arises from the polarization of the external dielectric medium. Thus if the charge, q, is displaced from the origin while the polarization of the medium remains fixed, as in the third model process (or, equivalently, if the origin in the second term is translated away from the position of q, as in the second model process), then work must be done. This work constitutes the electrostatic contribution to $U_{0,\mathrm{sr}}$ and its value is given by the product of q and that second term. After transformation of coordinates to attain consistency with the form of $U_{0,\mathrm{sr}}$ given in eq 5, it follows from eq 15 that

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(16) Equation 13 and 14 are exact if it is correct to make the common assumption that $\Delta G^{\ddagger 14}$ is identical with $\Delta G°$ for formation of the activated complex from reactants.

(17) E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 35 (1966).

(18) W. R. Smythe, "Static and Dynamic Electricity," 3rd ed, McGraw-Hill, New York, N. Y., 1968, Chapter 5.

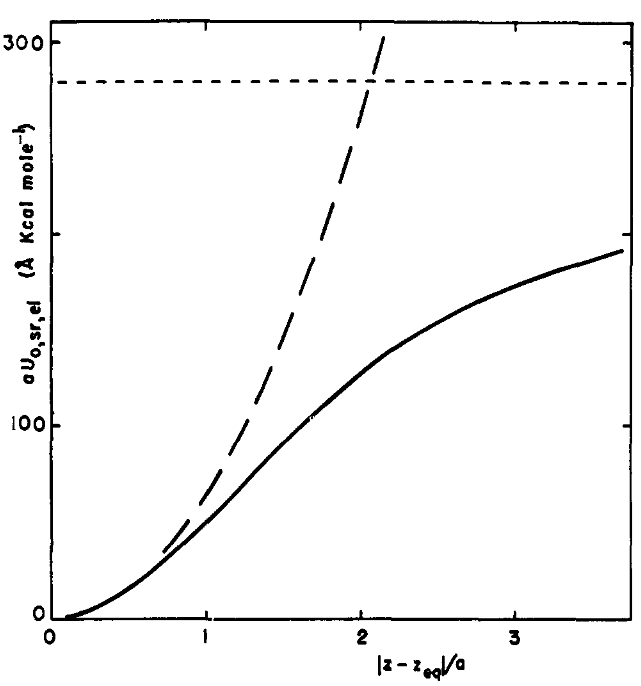

Figure 5. The solvent-derived potential well, $U_{0,\mathrm{sr,el}}$: (——) the exact function given by eq 17; (— —) the harmonic oscillator approximation calculated from eq 5 and 18; (- - -) the asymptote to the exact function.

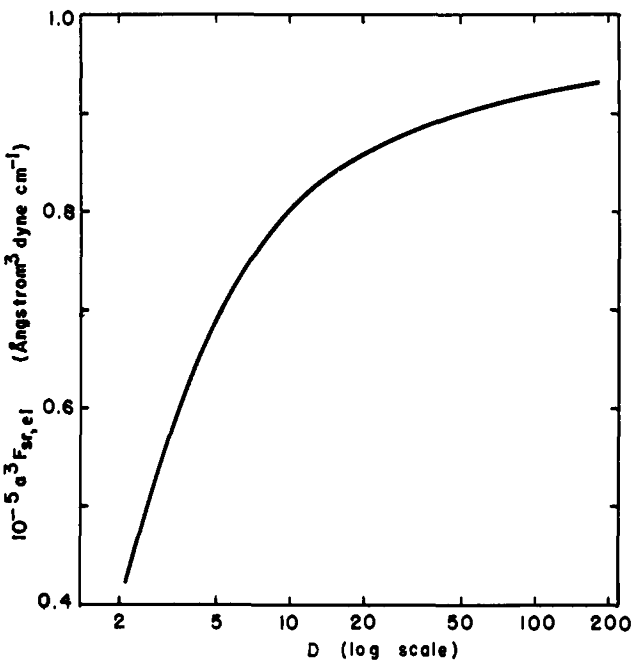

Figure 6. The solvent-derived force constant, $F_{\mathrm{sr,el}}$ (calculated from eq 18) as a function of the dielectric constant D. Note that a^3 $F_{\mathrm{sr,el}}$ is plotted in order to make the curve independent of the cavity radius.

the electrostatic contribution is given by

$$U_{0,\mathrm{sr,el}}(z - z_{\mathrm{eq}},\rho) = \frac{2q^2}{\pi}\int_0^\infty \frac{(D-1)kaK_0(ka)K_1(ka)I_0(k\rho)}{1+(D-1)kaI_0(ka)K_1(ka)} \times \{1-\cos[k(z-z_{\mathrm{eq}})]\}\,\mathrm{d}k \qquad (16)$$

Since the antisymmetric stretching vibration of the BHB′ system corresponds to a displacement of q along z while ρ remains equal to zero, the electrostatic contribution to $U_{0,\mathrm{sr}}$ for this vibration may be written in terms of the reduced displacement variable, $|z - z_{\mathrm{eq}}|/a$, as

$$U_{0,\mathrm{sr,el}}(z - z_{\mathrm{eq}},\ \rho = 0) = \frac{2q^2}{\pi a}\int_0^\infty \frac{(D-1)kaK_0(ka)K_1(ka)}{1+(D-1)kaI_0(ka)K_1(ka)} \times \{1-\cos[ka(|z-z_{\mathrm{eq}}|/a)]\}\,\mathrm{d}(ka) \qquad (17)$$

The corresponding force constant must be given by the value of $\partial^2(U_{0,\mathrm{sr,el}})/\partial z^2$ at the stationary point in $U_{0,\mathrm{sr,el}}$; thus

$$F_{\mathrm{sr,el}} = \frac{2q^2}{\pi a^3}\int_0^\infty \frac{(D-1)(ka)^3K_0(ka)K_1(ka)}{1+(D-1)kaI_0(ka)K_1(ka)}\,\mathrm{d}(ka) \qquad (18)$$

Numerical Evaluation of $U_{0,\mathrm{sr,el}}$ and $F_{\mathrm{sr,el}}$. The behavior of $U_{0,\mathrm{sr,el}}$ (eq 17) as a function of displacement along the cavity axis is illustrated and compared to that of the corresponding harmonic potential (eq 5 and 18) in Figure 5. In that figure, D has been set equal to 78, the static macroscopic dielectric constant of water at 25°, and the dependence of the potential function on the cavity radius has been taken into account implicitly by plotting $aU_{0,\mathrm{sr,el}}$ (a in ångströms) as a function of $|z - z_{\mathrm{eq}}|/a$ so that the curves shown are independent of a. It is evident from Figure 5 that the harmonic approximation to $U_{0,\mathrm{sr,el}}$ is very good for displacements whose magnitudes are no greater than the cavity radius.

In order to use this electrostatic model to predict observable behavior, it is necessary to assign values to a and D in eq 17 and 18. Consider first the choice of the cavity radius, a. The physical approximations inherent in the model are too great to allow the value of a to be determined *a priori* from molecular geometry. However, an appropriate value of a can be chosen through comparison of eq 17 to the equilibrium properties of the reactants. The depth, $U_{0,\mathrm{sr,el}}$ $(z - z_{\mathrm{eq}} = \infty)$, of the electrostatic solvent well is equal to $\Delta G_{\mathrm{sr,el}}$ for displacement of the charge from $z = z_{\mathrm{eq}}$ to $z = \infty$ while keeping the polarization fixed. Application of Marcus' general method for calculating electrostatic free energies of systems with nonequilibrium polarization[19] shows that the depth of that well is equal to *twice* the equilibrium ΔG for transfer of BHB′$^+$ from vacuum into solution. By setting D equal to the static dielectric constant of the solvent, the value of a which permits eq 17 to predict the correct ΔG for that transfer process can be calculated. Such an effective value of a will include compensations for many of the approximations in the model.

For reactions in aqueous solution, it is likely that proton transfers from H_3O^+ to small, unhindered bases (*e.g.*, H_2O or $CH_2{=}CHOR$) will be among those with the largest values of F_{sr}; no other singly charged acid would be expected to interact more strongly with the water structure than does H_3O^+. If Salomon's value,[20] $\Delta G° = -235$ kcal mol^{-1} at 25°, for the hydration of H_3O^+ is accepted, then the effective a calculated from eq 17 is 0.6 Å.

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(19) R. A. Marcus, *J. Chem. Phys.*, 38, 1858 (1963).
(20) M. Salomon, *J. Phys. Chem.*, 74, 2519 (1970).

Numerical integration of eq 18 yields the dependence of $F_{sr,el}$ on the dielectric constant D which is shown in Figure 6. For aqueous solutions ($D_s = 78$), $F_{sr,el} = 0.91 \times 10^5 a^{-3}$ dyn cm^{-1} where a is in ångströms.

Such an estimation of $F_{sr,el}$ from the static dielectric constant, D_s, implies the assumption that the entire polarization of the medium relaxes with a rate which is slow compared to the motion of the proton. This assumption cannot be correct for the electronic polarization and should be borderline for the vibrational polarization; only that fraction of the equilibrium solvation which accompanies an increase in D from D_{ir}, the infrared frequency dielectric constant, to D_s is expected to have a relaxation time which is very long compared to the duration of the proton-transfer event.

The value of $F_{sr,el}$ calculated above by setting $D = D_s$ in eq 18 is thus too high, and application of Marcus' analysis[19] shows that the correct value is

$$F_{sr,el} = F_{sr,el}(D_s) - F_{sr,el}(D_\nu) \tag{19}$$

where each term on the right hand side of eq 19 is evaluated from eq 18 (or Figure 6), and D_ν is the effective high frequency dielectric constant. The value of D_ν should lie between D_{ir} and D_{op}, the optical frequency dielectric constant. For water, D_{op} is 1.7 and D_{ir} lies between 1.7 and *ca.* 5.[21] If the median of this range, 3.3, is taken as an approximate value for D_ν, then the corresponding value of $F_{sr,el}$ for proton transfer from H_3O^+ is 1.5×10^5 dyn cm^{-1}; this estimate is uncertain by about a factor of 2 because of the range of uncertainty in D_ν and should be a rough upper limit on F_{sr}.

Estimation of F_{ch}. For the parabolic approximation to the chemical barrier, it follows from eq 4 that

$$-F_{ch} = 2\Delta U_0{}^{\ddagger}{}_{ch}/(z^{\ddagger}{}_{ch})^2 \tag{20}$$

and $z^{\ddagger}{}_{ch}$ is in turn given by

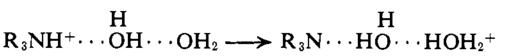
$$z^{\ddagger}{}_{ch} = z^p/(1 + \sqrt{(1 - (\Delta U_0{}^{\circ}{}_{ch}/\Delta U_0{}^{\ddagger}{}_{ch}))}) \tag{21}$$

where $\Delta U_0{}^{\circ}{}_{ch} = U_{0,ch}(z = z^p)$.

In assigning a value to z^p, it is important to recall that z measures displacement of the *charge* and not of the proton. The smallest possible values of z^p will correspond to reactions between simple saturated acids and bases without bridging water; *e.g.*

$$R_3NH^+\cdots OH_2 \longrightarrow R_3N\cdots HOH_2^+ \tag{22}$$

In such reactions z^p should be approximately equal to the distance between the basic atoms in the hydrogen-bonded complex; this distance varies from a minimum of 2.26 Å for HF_2^- (in solid KHF_2) to more than 3 Å.[22] Much larger values of z^p can correspond to reactions in which bridging water molecules intervene between the two bases, *e.g.*



$$R_3NH^+\cdots\overset{H}{O}H\cdots OH_2 \longrightarrow R_3N\cdots H\overset{H}{O}\cdots HOH_2^+ \tag{23}$$

or in which the charge on one of the acids or bases is centered far from the site of proton transfer, *e.g.*

$$ROCH{=}CH_2\cdots HOH_2^+ \longrightarrow RO^+{=}CHCH_3\cdots OH_2 \tag{24}$$

In either of these latter two examples, z^p would be expected to have a value near 6 Å.

For symmetric proton transfers between identical bases, $z^{\ddagger}{}_{ch}$ is equal to $^1/_2 z^p$. Only for very unsymmetric transfers will $z^{\ddagger}{}_{ch}$ be expected to vary widely from that value; *e.g.*, an exoergic reaction must be so unsymmetric that $-\Delta U_0{}^{\circ}{}_{ch} = 8\Delta U_0{}^{\ddagger}{}_{ch}$ before $z^{\ddagger}{}_{ch}$ (eq 21) is reduced by a factor of 2 to $^1/_4 z^p$. Thus $z^{\ddagger}{}_{ch}$ is expected to fall in the approximate range, 1–3 Å, for nearly symmetric reactions and to approach limits of 0 Å and z^p (*ca.* 2.2–6 Å) for values of $\Delta U_0{}^{\circ}{}_{ch} \ll 0$ and $\gg 0$, respectively.

This range of $z^{\ddagger}{}_{ch}$ leads to values of $|F_{ch}|$ (eq 20) which are smaller than the upper limit on $F_{sr,el}$ predicted above (1.5×10^5 dyn cm^{-1}); *e.g.*, for a reaction with $\Delta U_0{}^{\ddagger}{}_{ch} = 20$ kcal mol^{-1} and $\Delta U_0{}^{\circ}{}_{ch} = 0$, the corresponding range of $|F_{ch}|$ is 0.3×10^5–0.03×10^5 dyn cm^{-1}.

Estimation of τ. Conditions Leading to the Coupled Mechanism. The foregoing discussions have shown that, for proton transfer between small uncharged bases, the magnitude of $F_{sr,el}$ is likely to exceed that of F_{ch}; the transfer should thus proceed by either the second uncoupled mechanism or the coupled mechanism. Which of these mechanisms is followed is determined by the relative magnitudes of two possible contributions to $\Delta G^{\ddagger}$: (a) the second term in eq 14, $RT \ln (\tau kT/h)$, and (b) the difference between $\Delta U_0{}^{\ddagger}{}_{ch}$ and $\Delta U_0{}^{\ddagger}$ for the second uncoupled mechanism (eq 12). A comparison of these magnitudes requires a value for τ.

For bulk solvents, the microscopic dielectric relaxation time should not differ from the observable macroscopic dielectric relaxation time by more than a factor of 2.[23,24] However, the factor by which τ, the microscopic relaxation time in the neighborhood of the BHB′ complex, may differ from that in the bulk solvent is not known. In the absence of any observed values for τ, we may use macroscopic relaxation times to estimate the magnitude of the second term in eq 12. For H_2O at 20°, the observed macroscopic dielectric relaxation time is 9.55×10^{-12} sec,[21] and the corresponding value of $RT \ln (\tau kT/h)$ is 2.4 kcal mol^{-1}; each factor of 2 uncertainty in τ leads to an uncertainty of ± 0.4 kcal mol^{-1} in this term.

Thus to a first approximation for proton transfers in aqueous solution, whenever $\Delta U_0{}^{\ddagger}$ for the second uncoupled mechanism exceeds $\Delta U_0{}^{\ddagger}{}_{ch}$ by more than 2–3 kcal mol^{-1}, the coupled mechanism is likely to be followed. This criterion can be restated in terms of force constants if the approximation is made that $z^{\ddagger}{}_{eq} = z^{\ddagger}{}_{ch}$;[25] in that case, eq 12, 5, and 4 lead to

$$F_{sr} - |F_{ch}| = 2(\Delta U_0{}^{\ddagger} - \Delta U_0{}^{\ddagger}{}_{ch})/(z^{\ddagger}{}_{ch})^2 \tag{25}$$

For the most probable range of $z^{\ddagger}{}_{ch}$ estimated above, 1–3 Å, the inequality, $\Delta U_0{}^{\ddagger} - \Delta U_0{}^{\ddagger}{}_{ch} > 3$ kcal mol^{-1}, thus corresponds to a range of force constant inequalities, $F_{sr} - |F_{ch}| > 0.04 \times 10^5$–$0.005 \times 10^5$ dyn cm^{-1}, respectively.

Since a negative value of that force constant difference requires the reaction to follow the first uncoupled mechanism, the total range of that difference which permits the reaction to follow the second uncoupled mech-

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(21) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, New York, N. Y., 1969, Chapter 4, particularly pp 199–217.

(22) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, Chapter 9.

(23) F. Fatuzzo and P. R. Mason, *Proc. Phys. Soc.*, 90, 729, 741 (1967).

(24) S. H. Glarum, *J. Chem. Phys.*, 33, 1371 (1960).

(25) This is a very good approximation whenever the reaction is sufficiently symmetric that $z^{\ddagger}{}_{ch} \approx {}^1/_2 z^p$, since then eq 11 also requires that $z^{\ddagger}{}_{eq} \approx {}^1/_2 z^p$.

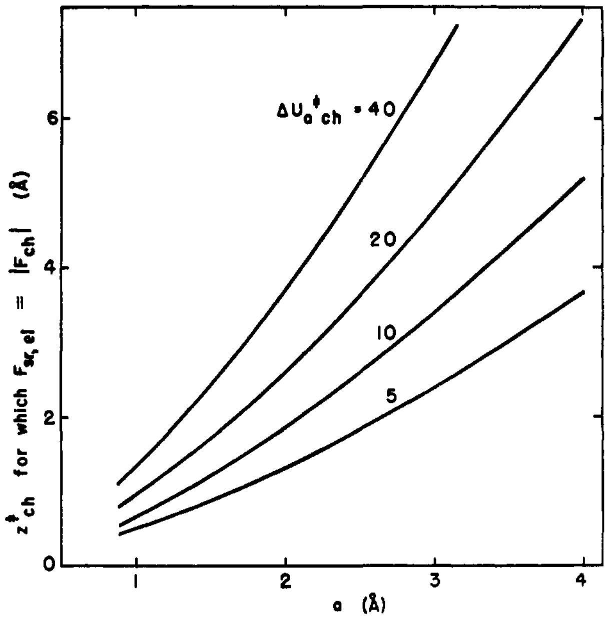

Figure 7. Division between mechanisms as a function of the cavity radius, *a*, the structure of the activated complex in the "chemical" mechanism, $z^{\ddagger}{}_{ch}$, and the potential energy of activation for the "chemical" mechanism, $\Delta U_0{}^{\ddagger}{}_{ch}$ (kcal mol^{-1}). For each $\Delta U_0{}^{\ddagger}{}_{ch}$, points below the curve represent systems in which transfers should follow the first uncoupled mechanism; points above the curve represent systems in which transfers should follow either the coupled or the second uncoupled mechanism.

anism is small in comparison to the possible individual ranges of $F_{sr,el}$ and F_{ch}. Most proton-transfer reactions are thus expected to follow either the coupled mechanism or the first uncoupled mechanism, and reactions following the second uncoupled mechanism (which is the only one for which the activated complex can have a nonequilibrated environment) should be rare.

Transfer between Charged Bases. The electrostatic model as described above is explicitly formulated to apply to proton transfer between uncharged bases. In such transfers (*e.g.*, eq 2, 22–24) contributions to the electrostatic potential which result from dipole or higher moments of the charge distribution should be much less important than the contribution which arises from the net positive charge, and such a model based on a point charge in a cavity should be a good first approximation. That model and eq 18 for $F_{sr,el}$ are equally applicable to the electrostatically equivalent case of proton transfer between two negatively charged bases, *e.g.*

$$\mathrm{HO^-\cdots HCH_2NO_2 \longrightarrow HOH\cdots CH_2NO_2^-} \qquad (26)$$

since proton transfer here corresponds to a translation of the center of negative charge.

For proton transfer between bases of unequal charge, that simple model is not applicable. For example, in

$$\mathrm{R_3N\cdots HCH_2NO_2 \longrightarrow R_3NH^+\cdots CH_2NO_2^-} \qquad (27)$$

there is no net charge on the BHB′ complex; the dominant contribution to $U_{0,sr,el}$ is expected to arise from the dipole moment, and the electrostatic consequence of proton motion is a change in that dipole moment. The magnitude of $F_{sr,el}$ thus varies with the extent of transfer; this variation makes quantitative predictions difficult and uncertain. However, the magnitude of $U_{0,sr,el}$ which results from a purely dipolar charge distribution will always be lower than that derived above from the point charge model for transfer between uncharged bases.

Summary of Predictions from the Electrostatic Model. The estimates of $F_{sr,el}$ and F_{ch} given above cover ranges which allow all three possible mechanisms for proton transfer. Which of these mechanisms is followed in any individual reaction depends on the sign and magnitude of the difference, $F_{sr} - |F_{ch}|$, between the magnitudes of these force constants, which in turn depends on three molecular parameters: (1) the steric bulk of the bases as reflected in the cavity radius *a;* (2) the distance through which the charge is transferred in the chemical activation process, $z^{\ddagger}{}_{ch}$; and (3) the internal potential energy increment accompanying the chemical activation process, $\Delta U_0{}^{\ddagger}{}_{ch}$. The values of $F_{sr,el}$ predicted by this model correspond to transfers between equally charged bases and are only upper limits for transfers between bases with unequal charge.

The transfer is predicted to follow the first uncoupled mechanism whenever $F_{sr} < |F_{ch}|$. This mechanism is thus expected for reactants which are sufficiently bulky (large *a*) and is favored whenever charge delocalization and/or bridging solvent molecules are absent (small $z^{\ddagger}{}_{ch}$) and when the reaction is observed to be slow (suggesting a large $\Delta U_0{}^{\ddagger}{}_{ch}$). Since the solvent configuration is predicted to be in equilibrium with the internal structure in both the initial and transition states for this mechanism, such reactions should have normal activation parameters, isotope effects, etc.

The reaction should follow either the coupled or the second uncoupled mechanism whenever $F_{sr} > |F_{ch}|$; as discussed above, the coupled mechanism is expected to be by far the more common of these two. Either can lead to the observation of abnormal activation parameters and isotope effects. Figure 7 shows the divisions (*i.e.*, the curves along which $F_{sr,el} = |F_{ch}|$) between the regions of *a* and $z^{\ddagger}{}_{ch}$ which for various $\Delta U_0{}^{\ddagger}{}_{ch}$ lead to the two directions of inequality between these force constants for reaction in aqueous solution. For any given $\Delta U_0{}^{\ddagger}{}_{ch}$, all $(a, z^{\ddagger}{}_{ch})$ points which lie below the curve (large *a* and small $z^{\ddagger}{}_{ch}$) correspond to the first uncoupled mechanism, while all points above the curve (smaller *a* and larger $z^{\ddagger}{}_{ch}$) correspond to the coupled and second uncoupled mechanisms. Both of these regions contain wide ranges of physically reasonable values of *a* and $z^{\ddagger}{}_{ch}$, so that both types of mechanisms are predicted to be common.

The improbability of any mechanism in which the solvent remains in the configuration which is characteristic of reactants while the proton is transferred is shown dramatically by the numerical values for $\Delta U_{0,sr,el}$ which are given by eq 17 or Figure 5. Thus in aqueous solution even for a cavity radius as large as 3 Å, to shift the charge away from the minimum in the solvent well by 1.5 Å (a conservative value for $z^{\ddagger}$)[26] would cost 6 kcal mol^{-1}; the rate *via* this mechanism would then be 5×10^{-5} times the rate *via* the first uncoupled mechanism or *ca.* 3×10^{-3} times the rate *via* the coupled mechanism. For the H_3O^+ model with $a = 0.6$ Å, the rate factor relative to the first uncoupled mechanism becomes 10^{-18}. Even after correction for the rapidly relaxing electronic and vibrational contributions to

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(26) For such a mechanism, $z^{\ddagger}$ will always exceed $z^{\ddagger}{}_{ch}$ and will equal z^{p} unless $-\Delta G^{\circ}$ exceeds $\Delta U_{0,sr,el}$ ($[z - z_{eq}] = z^{p}$).

the polarization, these rate factors remain prohibitively small.

Comparison to Experimental Observations

An ideal experimental system for testing the predictions of this theory would be one in which the structure of the reactants was varied over a sufficiently wide range to include both predicted mechanistic extremes: coupled and first uncoupled mechanisms. Such a system should show discontinuities in the behavior of observed parameters as the structure of the reactants is varied through the point at which $F_{sr} = |F_{ch}|$. Unfortunately, few systems have been studied which approach this ideal, and the aproximations inherent in the calculation of F_{sr} and $|F_{ch}|$ prevent the confident *a priori* prediction of which is larger for isolated reactions.

Nevertheless, many examples do exist which are in qualitative agreement with this theory. Several examples of surprising or apparently aberrant observations are discussed below. Each has, in the past, required its own *ad hoc* rationale. The present theory provides a unified explanation for these diverse observations.

Proton Tunneling. One of the closest approaches to the ideal system described above is provided by observations[27,28] on proton abstraction from 2-nitropropane by pyridine bases. In a series of abstractions by ten methyl-substituted pyridines, Lewis and Funderburk[27b] found strong evidence for tunneling only when the 2,6 positions on the pyridine were both methylated; pyridine and substituted pyridines in which at least one of these positions was unsubstituted gave no evidence for tunneling. The original explanation for this observation was that steric strain arising from interaction between the methyl groups on the nitropropane and those on the 2,6-disubstituted pyridine tends to make the barrier high and narrow, thus favoring tunneling.

According to the present theory, these observations require no special explanation. The relevant prediction here is that tunneling should be suppressed whenever the coupled mechanism is followed (*i.e.*, whenever $F_{sr} \gg |F_{ch}|$). This suppression results from the fact that tunneling is a form of rapid proton transfer and thus *must* occur by way of an uncoupled mechanism.[29] Whenever the coupled mechanism is the most favorable path for transfer without tunneling, then $F_{sr} \gg |F_{ch}|$ and any tunneling would have to be *via* the second uncoupled mechanism; the twin barriers in this latter mechanism are higher than the barrier which must be crossed in the coupled mechanism and tunneling thus carries a heavy handicap.

The data for these abstractions by pyridine bases thus suggest that $F_{sr} < |F_{ch}|$ when the pyridine is 2,6-disubstituted, and $F_{sr} > |F_{ch}|$ otherwise. This agrees with the qualitative prediction of the electrostatic model; the four methyl groups present in the BHB′ complexes for 2,6-dimethylpyridines exclude solvent, leading to a large effective cavity radius a and a very low value of $F_{sr,el}$ (which varies as the inverse *cube* of a). Increasing steric contributions to $\Delta U_0{}^{\ddagger}{}_{ch}$ would also tend to make $F_{sr} < |F_{ch}|$ by increasing $|F_{ch}|$ (eq 20).

Evidence concerning proton tunneling in most other systems does not lend itself to such simple and clear interpretation.[30] However, the general problem has not been to explain why tunneling is sometimes observed, but rather to explain why experimental evidence for tunneling is so rare. The present theory, by restricting tunneling to reactions for which $F_{sr} < |F_{ch}|$, accounts for this rarity. Factors which have been identified as favoring tunneling[30] are just those which should decrease F_{sr} or increase $|F_{ch}|$; *e.g.*, steric bulk (large a), steric strain (large $|F_{ch}|$), aqueous solvent (large D_{ir}), and strong hydrogen bonding (small $z^{\ddagger}$). Also, the lack of evidence for tunneling in the extensively studied area of transfers from H_3O^+ to uncharged carbon bases is in accord with the prediction that such transfers are likely to occur *via* the coupled mechanism.

Entropies of Activation. It has been pointed out by Kreevoy[2] that the values of $\Delta S^{\ddagger}$ observed for proton transfer from H_3O^+ to such bases as vinyl ethers and vinylmercuric halides are all more negative than expected by 5–10 eu. Such low $\Delta S^{\ddagger}$ values are readily explained if these reactions follow the coupled mechanism (as is expected for transfers from H_3O^+). For a bimolecular reaction which is not diffusion controlled, the observed $\Delta S^{\ddagger}$ is a sum of $\Delta S°_1$ (for the association step, eq 1) and $\Delta S^{\ddagger}{}_2$ (for the activation process in the transfer event, eq 2). $\Delta S°_1$ will be approximately constant and equal to the "cratic"[31] or localization entropy ($-R \ln 55 = -8$ eu in H_2O) with perhaps a small additional negative contribution arising from loss of rotational freedom. $\Delta S^{\ddagger}{}_2$ will depend on the mechanism of the transfer event; it will be equal to $\Delta S^{\ddagger}{}_{ch}$ (for the hypothetical chemical mechanism) if the first uncoupled mechanism is followed; it will, however, from eq 14 be equal to $\Delta S^{\ddagger}{}_{ch} - R\,\partial(T \ln [\tau kT/h])/\partial T$ if the coupled mechanism is followed.[32] If the reorientational relaxation time, τ, of the solvent in the neighborhood of reactants is assumed to be nearly independent of temperature,[33] then for the coupled mechanism

$$\Delta S^{\ddagger}{}_2 = \Delta S^{\ddagger}{}_{ch} - R[\ln(\tau kT/h) + 1] \qquad (28)$$

Assuming τ to have a value which is of the same order of magnitude as the macroscopic dielectric relaxation time of water at the temperature of maximum density (1.5×10^{-11} sec)[21] thus leads to the prediction that the coupled mechanism should lead to an observed $\Delta S^{\ddagger}$ which is about 11 eu more negative than would be observed if the first uncoupled mechanism were followed. If τ is assumed to decrease slightly with increasing temperature instead of remaining constant, then the predicted extent of deviation from ΔS_{ch} will be smaller and 11 eu will be a rough upper limit on that deviation. Either

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(27) (a) E. S. Lewis and J. D. Allen, *J. Amer. Chem. Soc.*, **86**, 2022 (1964); (b) E. S. Lewis and L. H. Funderburk, *ibid.*, **89**, 2322 (1967).

(28) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

(29) The mechanism for proton transfer *via* tunneling is thus very much like the Marcus mechanism[8] for electron transfer: solvent reorganization into an intermediate configuration, followed by tunneling of the proton between the two possible sites, and finally solvent relaxation.

(30) See, for example, E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969).

(31) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill, New York, N. Y., 1953, Chapter 5.

(32) For the presumably rare second uncoupled mechanism, $\Delta S^{\ddagger}{}_2$ is less directly predictable; it will be equal to $-R \ln 2$ plus the value of $\Delta S°$ for reorganization of solvent from the configuration for $z = 0$ to that for $z = z^{\ddagger}{}_{eq}$. Since $z^{\ddagger}{}_{eq}$ cannot deviate far from $z^{\ddagger}{}_{ch}$ without having the reaction switch from the second uncoupled to the coupled mechanism, $\Delta S^{\ddagger}{}_2$ should be approximately equal to $\Delta S^{\ddagger}{}_{ch} - R \ln 2$ minus any internal contribution to $\Delta S^{\ddagger}{}_{ch}$.

(33) These assumptions are consistent with the common view that organic solutes in water stabilize regions of water structure in their neighborhoods which are in some sense characteristic of cold water.

assumption leads to qualitative agreement with the observed deviation of −5 to −10 eu.

Solvent Effects and Solvent Isotope Effects. Equation 13 predicts that the rate constant for a proton-transfer reaction which follows the coupled mechanism will be proportional to τ^{-1}. When the solvent is varied, it is probable that τ will vary in approximate proportion to the macroscopic dielectric relaxation time of the solvent. The observed solvent effect on the rate of such reactions should thus be a product of two factors: (1) a normal solvent effect of the same kind as that which should affect an equilibrium constant, and (2) the inverse ratio of the dielectric relaxation times for the two solvents.

A scarcity of data prevents an extensive test of this prediction. However, one solvent pair exists for which are known both the ratio of the dielectric relaxation times and the solvent effect on the rates of several proton-transfer reactions: D_2O and H_2O. Since the static dielectric constants of D_2O and H_2O are nearly identical, the relaxation time ratio is expected to be the dominant factor in the solvent isotope effect on the rate of the coupled mechanism.

Bell[3] has called attention to the observation that the value of $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$ for proton- or deuteron-transfer reactions is nearly always between 1.2 and 1.4. The reactions to which he refers are of the type which is likely to follow the coupled mechanism. Since the observed ratio of the macroscopic dielectric relaxation times for these solvents at 25° is $\tau_d(D_2O)/\tau_d(H_2O) = 1.28$, this observation is in good agreement with the prediction of the present theory.

Primary Isotope Effects. The solvent-derived potential well $U_{0,\mathrm{sr}}$, should be present for any vibrational motion which changes the internal charge distribution and whose frequency is greater than τ^{-1}. The corresponding force constant, F_{sr}, will add to the force constant which would characterize the vibration if solvent relaxation were fast. The presence of slowly relaxing solvent will thus change vibrational frequencies and isotope effects on rates and equilibria.

The total force constant for the antisymmetric stretch of the $\mathrm{BHB'^+}$ system in the transition state is given by $F_{\mathrm{sr}} - |F_{\mathrm{ch}}|$. In the coupled mechanism, this difference is positive, and since the hydrogen being transferred is always in a potential well, the isotope effect observed for proton *vs.* deuteron transfer is really a secondary effect. The value of this total force constant should range up to the maximum value of *ca.* 1.5×10^5 dyn cm^{-1} estimated for F_{sr}. The corresponding frequency is about 1600 cm^{-1} which predicts a maximum inverse zero-point energy contribution to the observed $k_{\mathrm{H}}/k_{\mathrm{D}}$ of about a factor of 3.

Similar contributions to observed kinetic isotope effects from the perturbation of ground state vibrations by $U_{0,\mathrm{sr}}$ should be small, since probable ground state values of F_{sr} are small in comparison to the force constants which arise from internal bonding. The force constant for the $\mathrm{B{-}H^+}$ stretch in the ground state will be of the order of 5×10^5 dyn cm^{-1}. If the maximum value of $F_{\mathrm{sr,el}}$ estimated above were added to this, it would produce a change in frequency of *ca.* 14% and would increase the observed $k_{\mathrm{H}}/k_{\mathrm{D}}$ for proton transfer from $\mathrm{BH^+}$ by a factor of about 1.34 (for $\bar{\nu} \approx 3000$ cm^{-1}). However, such ground state vibrations correspond more closely to changing a dipole moment than to translating a charge and therefore should be associated with values of F_{sr} which are much smaller than that maximum. This prediction is supported by the common observation that solvent effects on observed vibrational frequencies are small.

In summary, "primary" isotope effects observed for proton transfers between small bases should be smaller than would be expected from the internal structures of the reactants and the activated complex. For example, $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{I}}$, the primary contribution to the rate constant ratio for transfer from H_3O^+ *vs.* D_3O^+, is predicted to be decreased by a factor which could be as large as 3. This prediction is in good agreement with observation; values of $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{I}}$ are often well below the expected maximum even when other evidence suggests that the activated complex is nearly symmetric; values near 5 are common in such cases. Kresge and Chiang[34] have explicitly called attention to such low values.

Deviations from Brønsted Correlations. The number of plausible factors which have been proposed to explain scatter in Brønsted correlations is already more than sufficient to account for the observed scatter. It is thus difficult to ascertain the extent to which the existence of three distinct mechanisms for the transfer event might contribute to most such deviations.

One commonly observed deviation, however, is in particularly good agreement with the present predictions. Many workers[2b,4,35–37] have commented on the fact that the rate constant for transfer from H_3O^+ to various uncharged bases is lower than that predicted from the pK_a of H_3O^+ (−1.7) in combination with the Brønsted correlation based on transfer from uncharged acids. The extent of the observed deviation is usually a factor which lies between 10 and 100. The transfer from H_3O^+ is expected to follow the coupled mechanism, while the transfers from the uncharged acids should have much lower values of F_{sr} and thus might well follow the first uncoupled mechanism. Equation 13 predicts that a transfer *via* the coupled mechanism will be slower than a transfer over the same chemical barrier *via* the first uncoupled mechanism by the factor $\tau kT/h$. The value of this factor was estimated above to be within a factor of 2 of 60 in good agreement with the observed deviations of $k_{\mathrm{H_3O^+}}$.

Ultrafast Proton Transfers. The existence of proton transfers within hydrogen bonded complexes (eq 2) which have rate constants of the order of 10^{13} sec^{-1} has been discussed in detail by Grunwald.[1b] In the context of the present discussion, such transfers must be described as occurring *via* an uncoupled mechanism, and the high rate constants must refer to the transfer event *per se*.

Most transfers which appear to proceed with such ultrafast rates are of a charge type (*e.g.*, $H_2O + HClO_4$) which is predicted to have low values of F_{sr}, and all have negative values of $\Delta G°$. These transfers can thus follow a variant of the uncoupled mechanism in which the solvent never relaxes into the equilibrium configura-

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(34) A. J. Kresge and Y. Chiang, *J. Chem. Soc. B*, 58 (1967).

(35) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, p 93.

(36) A. J. Kresge, L. E. Hakka, S. Mylonakis, and Y. Sato, *Discuss. Faraday Soc.*, 39, 75 (1965).

(37) M. M. Kreevoy, T. S. Straub, W. V. Kayser, and J. L. Melquist, *J. Amer. Chem. Soc.*, 89, 1201 (1967).

tion for the unstable (*e.g.*, $H_2O\cdots HClO_4$) state. This mechanism is more easily described in terms of the slower reverse reaction. In that reverse, the solvent first reorganizes from the configuration which is in equilibrium with the reactants ($H_2OH^+\cdots OClO_3^-$) into an intermediate configuration, the proton then transfers to give $H_2O\cdots HOClO_3$, but before the solvent can relax, the proton is transferred back to form reactants. It is this back transfer event which is ultrafast.

In contrast, the $H_2O + H_3O^+$ reaction is not ultrafast. This reaction should have a large F_{sr} and should thus follow the coupled mechanism. In fact, its rate constant (2×10^{11} sec^{-1} at 25° after correction to a per proton basis)[1b] is within a factor of 2 of the reciprocal of the macroscopic dielectric relaxation time for water (1.2×10^{11} sec^{-1}). It would appear that this reaction proceeds as fast as it can *via* the coupled mechanism (*i.e.*, with $k \approx \tau^{-1}$).

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A Comparison of Diborane Molecular Properties from Minimum Basis Set and Extended Slater Orbital Wave Functions

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Abstract: A comparison of extended and optimized minimum STO basis set wave functions for B_2H_6 indicates that boron hydride energies, ionization potentials, diamagnetic susceptibility and shielding constants, and total electron densities may be reliably determined from a minimum basis set calculation. Minimum basis set difference densities and nuclear quadrupole coupling constants are only qualitatively correct. Minimum basis set atomization energies appear to be more accurate than those computed with large basis sets, when the atomic wave functions are determined using the molecular exponents.

The study of diborane (B_2H_6) by self-consistent field (SCF) methods has been the subject of much theoretical work.[1-10] As the prototype boron hydride, B_2H_6 is the simplest stable member of a large class of molecules whose chemical and physical properties have long fascinated chemists. The nature of electron-deficient bonding, the anomalous character of chemical shifts,[11,12] the mechanism of molecular rearrangements,[13] and the interpretation of chemical reactivity[14] have all inspired much theoretical research and speculation.

Most of the previous boron hydride SCF calculations have been done with minimum basis set wave functions. Because a boron hydride minimum basis set provides a favorable ratio (2:1) of basis orbitals to occupied orbitals, it has been hoped that improvement of the wave function would be unnecessary for the investigation of most boron hydride properties. The present study was undertaken in order to test the adequacy of the minimum basis set approximation.

Wave Functions

A discussion of the minimum basis set wave function chosen for purposes of comparison has been given in a previous paper.[5g] The basis consists of a 1s, 2s, 2p (three isotropic components) set of Slater-type orbitals (STO's) on each boron and a 1s STO on each hydrogen. The exponent of each orbital has been optimized with the total SCF energy as the variational criterion.

The expanded basis set reported here consists of 68 STO's, 19 on each boron and 5 on each hydrogen. The basis orbitals for both the minimum and expanded basis sets are given in Table I. For the large basis set, exponents of s and p orbitals on boron are

(1) V. Schomaker, *J. Chim. Phys. Physicochim. Biol.*, **46**, 262 (1949).

(2) (a) H. C. Longuet-Higgins, *ibid.*, **46**, 268 (1949); (b) *J. Roy. Inst. Chem.*, 77, 197 (1953).

(3) K. S. Pitzer, *J. Amer. Chem. Soc.*, **67**, 1126 (1945).

(4) R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949).

(5) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963; (b) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954); (c) R. Hoffmann and W. N. Lipscomb, *ibid.*, 37, 2872 (1962); (d) M. D. Newton, F. P. Boer, W. E. Palke, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **53**, 1089 (1965); (e) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966); (f) W. E. Palke and W. N. Lipscomb, *J. Chem. Phys.*, **45**, 3948 (1966); (g) E. Switkes, R. M. Stevens, M. D. Newton, and W. N. Lipscomb, *ibid.*, **51**, 2085 (1969).

(6) W. C. Hamilton, *Proc. Roy. Soc., Ser. A*, **235**, 395 (1956).

(7) M. Yamazaki, *J. Chem. Phys.*, **27**, 1041 (1957).

(8) L. Burnelle and J. J. Kaufman, *ibid.*, **43**, 3540 (1965).

(9) R. T. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *ibid.*, **45**, 2835 (1966).

(10) C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Amer. Chem. Soc.*, 92, 3863 (1970).

(11) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(12) (a) T. Onak, D. Marynick, P. Mattschei, and G. Dunks, *Inorg. Chem.*, 7, 1754 (1968); (b) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1797 (1969); T. Onak and D. Marynick, *Trans. Faraday Soc.*, **66**, 1843 (1970).

(13) (a) T. Onak, L. B. Friedman, J. A. Hartsuck, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 3439 (1966); (b) H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *ibid.*, **89**, 4218 (1967); (c) H. V. Hart and W. N. Lipscomb, *ibid.*, **91**, 771 (1969); (d) W. N. Lipscomb, *Science*, **153**, 373 (1966).

(14) (a) T. F. Koetzle and W. N. Lipscomb, *Inorg. Chem.*, 9, 2743 (1970); (b) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 92, 7019 (1970); (c) E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens, and W. N. Lipscomb, *ibid.*, 92, 3837 (1970); (d) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, 10, 171 (1971).