preceding paper in this issue.[22] For extinction coefficient measurements the diphenylketyl radical was generated by either abstraction from cyclohexane solvent or by abstraction from 1,4-cyclohexadiene in cyclohexane. For bleaching quantum yields only the former source of the radical was used in order to eliminate potential problems due to diene quenching of the excited radical.

Detection of Hydrogen by Raman Spectroscopy. Samples of 6.6 mM benzophenone in cyclohexane (2 mL) in 7 × 7 mm^2 quartz cells were nitrogen purged and then irradiated with 750 308-nm laser shots and 750 pairs of 308- and 515-nm pulses. The samples were shaken every 20 shots. The gas above the photolyzed samples was then analyzed by Raman spectroscopy for hydrogen and cyclohexane. The experimental setup for measuring Raman spectra has been previously described.[44]

Acknowledgment. Thanks are due to Drs. H. L. Casal and W. F. Murphy for the Raman experiment, to D. Lindsay for LC/MS measurements, and to S. E. Sugamori for technical assistance.

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Structure Sensitivity of the Marcus λ for Hydride Transfer between NAD^+ Analogues[1]

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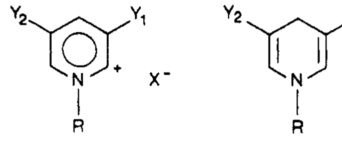
Abstract: Thirty-five rate constants, k_{ij}, for transfer of hydride between various pyridinium, quinilinium, acridinium, and phenanthridinium ions spanning a range of over 10^{11} in their equilibrium constants K_{ij} and over 10^6 in k_{ij} have been measured. (All these ions can be regarded as analogues of NAD^+.) Calculation of these k_{ij} by conventional Marcus theory, with a constant, averaged value of the intrinsic barrier, λ, gives a fair level of agreement, with an average discrepancy of 0.9 between calculated and observed values of ln k_{ij}. Use of a structure-sensitive λ reduces this discrepancy to 0.5. The structure-sensitive λ is evaluated by using different values of λ, λ_n, for the symmetrical reactions of each cation. The λ_n depend on the ring system in a way that was determined experimentally and on the equilibrium constant for the reduction of the cation by a reference substance, 10-methylacridan, $K_{ij}{}^{\circ}$. The relation between λ_n and ln $K_{ij}{}^{\circ}$ is grounded in Marcus theory and permits the experimental determination of the tightness parameter, τ. In the present case the value of τ, 0.81, suggests the net loss of 19% of the initial carbon–hydrogen binding energy in the critical configuration and 19% excess negative charge on the in-flight hydrogen. The theory also suggests subsets of the data that should give good Brønsted curves and permits the estimation of their slopes, α. The estimated slopes are in reasonable agreement with experiment. The agreement between calculation and experiment supports the Marcus cross relation and the derived relation between λ_n, $K_{ij}{}^{\circ}$, and τ. It also provides some experimental support for the theoretically predicted variation of α with K_{ij}, although the effect is small. The Marcus theory is based on a model in which all the reactions in question proceed through the same general mechanism, involving no high-energy intermediates. Its success strongly suggests that these conditions are met.

In the semiempirical calculation of rate constants for atom or group transfer by Marcus theory[2-7] the rate constants for the related symmetrical (or degenerate) transfer reactions play a key role.[6] In this theory, both in its original form[2-5] (in which it is a quadratic free energy relationship) and in its modified form[6,7] (in which it includes cubic terms), the reactive event is divided into three stages: (1) reactants form a precursor configuration or complex, which may or may not be metastable; (2) the precursor is converted, by passing through a critical configuration,[8] to a successor complex or configuration; and (3) the successor is converted to the ultimate products. The free energy of activation for the second stage is modeled in terms of its free energy of reaction, $\Delta G^{\circ\prime}$, and the free energies of activation for the symmetric analogue reactions, $\lambda_i/4$ and $\lambda_j/4$.

Chart I



1 1H

compd	R	Y_1	Y_2	X
a	$C_6H_5CH_2$	CN	H	Br
b	$C_6H_5CH_2$	$COCH_3$	H	Br
c	$C_6H_5CH_2$	CO_2CH_3	H	Br
d	$C_6H_5CH_2$	$CONH_2$	H	Br
e	CH_3	$CONHCH_2C_6H_5$	H	I
f	CH_3	$CONHC_8H_{17}$	H	I
g	CH_3	CO_2CH_3	CO_2CH_3	I
h	$4\text{-}FC_6H_4CH_2$	CN	H	Br
2	$4\text{-}FC_6H_4CH_2$	$COCH_3$	H	Br
j	$4\text{-}FC_6H_4CH_2$	CO_2CH_3	H	Br
k	$4\text{-}FC_6H_4CH_2$	$CONH_2$	H	Br

In this paper we discuss hydride-transfer reactions of the type shown in eq 1, with rate constant k_{ij} ($\tilde{k}$ is Boltzman's constant,

$$A_i^+ + A_jH \rightarrow A_iH + A_j^+ \tag{1}$$

$$\Delta G^* = W^r + \lambda/4 + \Delta G^{\circ\prime}/2 + \Delta G^{\circ\prime 2}/4\lambda \tag{2}$$

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[8] The term "critical configuration" is used for the structure that, along with the reactant structures, determines the structure-related quantities, such as the Brønsted α and Hammett ρ, obtainable from k_{ij} measurement. It replaces the term "transition state", which we reserve for the structure corresponding to the point of maximum energy on the minimum energy path connecting reactants and products. The critical configuration can be different from the transition state because of tunneling and may not lie on the minimum energy path at all.[27]

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$$\Delta G^{\circ\prime} = \Delta G^{\circ} - W^{r} + W^{p} \tag{3}$$

$$\lambda = (\lambda_i + \lambda_j)/2 \tag{4}$$

$$k = \tilde{k}T/h \exp(-\Delta G^{*}/RT) \tag{5a}$$

$$K = \exp(-\Delta G^{\circ}/RT) \tag{5b}$$

k is a rate constant, K is an equilibrium constant, W^r is the standard free energy of formation of the precursor configuration from the reactants, and W^p is the standard free energy of formation of the successor configuration from the products. The standard free energy of the overall reaction is ΔG°, and eq 3 defines $\Delta G^{\circ\prime}$. The free energy of activation for the second state of an *energetically* symmetrical variant of the reaction shown in eq 1 is $\lambda/4$ and is called the intrinsic barrier. The intrinsic barriers for the *structurally* symmetrical variants of the reaction are $\lambda_i/4$ and $\lambda_j/4$, jointly symbolized by $\lambda_n/4$. They can be obtained from the rate constants for symmetrical reactions, k_{ii} or k_{jj}, jointly symbolized by k_{nn}, once a value has been assigned to W^r. The other symbols have their usual significance.) The hydride acceptors, A_i^+ and A_j^+, jointly symbolized by A_n^+, can all be regarded as analogues of the biochemical oxidizing agent nicotinamide adenine dinucleotide, NAD$^+$. They are substituted pyridinium ions (**1**), quinolinium ions (**2**), acridinium ions (**3**), or phenanthridinium ions (**4**) (Charts I–III). All rate constants were measured in dilute solution, at 25 °C, in a solvent consisting of four parts of 2-propanol to one part of water, by volume. We have established[6,7] and shall maintain the convention that A_i^+ is the oxidizing agent (hydride acceptor) when the reaction is written in the forward (not necessarily spontaneous) direction. For such reactions, Marcus theory leads to eq 2–4, which give their standard free energies of activation, ΔG^{*}, in terms of three interpretable quantities, W^r, λ, and $\Delta G^{\circ\prime}$. W^r is usually regarded as structure insensitive and accounts for that part of ΔG^{*} which is insensitive to variation in K. If A_i^+ and A_j^+ are structurally related, and of the same charge type, as they are in all the cases discussed in the present paper, it is reasonable that W^r and W^p should be similar in magnitude, and they are assumed to be equal. In that case $\Delta G^{\circ\prime}$ is equal to ΔG°, for which many experimental values are available.[6,9] W^r is the standard free energy of a process involving no covalency changes. The standard free energy for combining the two, independently mobile, reactant molecules into a single unit, reducing the number of large-excursion degrees of freedom, has been estimated to be 8 kJ mol^{-1},[4] and this value has been assigned to W^r in previous work on hydride transfer.[6,10] In the present paper, however, we have thought it advisable to use a small *negative* value for W^r, for reasons that are given below. As long as the value is small and constant, the exact value chosen has little effect on the final calculated rate constants, because an increase in W^r leads to an equal decrease in $\lambda/4$. This leaves only λ to be evaluated, using eq 4.

In applying Marcus theory to proton-transfer reactions, λ was assumed to be constant within a family of reactions and treated as an adjustable parameter.[4,11] Since, in the present case, there is no objective way to distinguish A_i from A_j, the assumption of constant λ would require that all λ_n be the same. Measured values showed that this was not the case. Values of k_{nn} seemed to vary both with structural subtype (pyridinium ion, quinolinium ion, etc.)[10] and also, within a subtype, with the value of the equilibrium constant for reduction of the A_n^+ in question by a standard hydride donor, K_{ij}°.[6] Closer examination of the theory then showed that the k_{nn} should be approximately linear functions of K_{ij}°, the slope giving information about the tightness[12] of the critical complex.[6,13] The expected relations are shown in eq 6 and 7. The sum of the

$$\mathrm{d}(\ln k_{ii})/\mathrm{d}(\ln K_{ij}^{\circ}) = \tau - 1 \tag{6}$$

$$\mathrm{d}(\ln k_{jj})/\mathrm{d}(\ln K_{ij}^{\circ}) = -(\tau - 1) \tag{7}$$

bond orders to the in-flight hydrogen at the critical configuration is τ[12]. If eq 6 and 7 are valid for each subfamily of compounds, i.e., pyridinium ions, quinolinium ions, phenanthridinium ions, etc., and τ is approximately constant, then λ can be calculated for any reaction of the type shown in eq 1, provided that τ has been determined and a symmetrical rate constant has been measured for at least one member of each of the subfamilies represented by A_i^+ and A_j^+. This permits a calculation of ln k_{ij} from eq 2 and 5a. In addition, eq 8 and 9 predict the sensitivity

$$\frac{\mathrm{d}(\ln k_{ij})}{\mathrm{d}(\ln K_{ij})} = \chi + \tfrac{1}{2}(\tau - 1) - \frac{1}{2}\left(\frac{RT \ln K_{ij}}{\lambda}\right)^2 (\tau - 1) \tag{8}$$

$$\frac{\mathrm{d}(\ln k_{ij})}{\mathrm{d}(\ln K_{ji})} = \chi - \tfrac{1}{2}(\tau - 1) + \frac{1}{2}\left(\frac{RT \ln K_{ij}}{\lambda}\right)^2 (\tau - 1) \tag{9}$$

$$\chi \equiv \frac{1}{2}\left(1 - \frac{RT \ln K}{\lambda}\right) \tag{10}$$

of ln k_{ij} to changes in ln K_{ij}.[6,13] It is the purpose of this paper to test the applicability of eq 2, 4, and 6–10 to hydride-transfer reactions. We will also test the idea that different ring systems generate inherently different values of λ. The K in eq 10 is either K_{ij} or K_{ji}, as appropriate. Equations 8 and 9 were obtained by using eq 2–5 to express ln k_{ij} as a function of W^r, λ, and ln K_{ij} and then differentiating.[6,13] Testing these equations tests the theory as a whole.

Experimental Section

"Symmetrical" exchange rates were newly measured for two quinoline derivatives and three pyridine derivatives. We could not measure the rates of reactions that were truly structurally symmetrical, so 1-trideuteriomethyl compounds were used as analogues of 1-methyl compounds, 1-(4-fluorobenzyl) compounds were used as analogues of benzyl compounds, and a 1-[3-(trifluoromethyl)benzyl] compound was used as an analogue of the 1-(4-cyanobenzyl) compound. In all cases the D-containing compounds were used as the oxidizing agents, but the fluorinated compounds could be used either as oxidizing agents or as reducing agents. These analogues made it possible to monitor the progress of the reactions by ^{1}H or ^{19}F NMR spectroscopy.

In the case of a reduced CH_3 compound reacting with an oxidized CD_3 compound, aliquots of 10–20 cm^3 were periodically removed from the reaction mixture, diluted with 50 cm^3 of water to reduce the solubility of the reduced compound, and equilibrated with 3-cm^3 samples of $CDCl_3$. The neutral reduced compounds were largely transferred to the $CDCl_3$ layer, while the ionic oxidized material remained in the aqueous phase. The organic layer was separated, washed with water to remove 2-propanol, and dried over anhydrous $MgSO_4$. The ^{1}H NMR spectrum of the $CDCl_3$ solution was obtained and the intensities of the CH_3-related and CH_2-related bands were evaluated by integration. The ratio of these two intensities, R, is initially 1.5 and decreases steadily as the reaction proceeds. (The CD_3 compound and the CH_3 compound both contain an identical CH_2 group, so the abundance of this group does not change as the reaction proceeds, and the intensity of its signal is a measure of the total abundance of CH_3 plus CD_3.) Rate constants, k_{nn}, were obtained graphically, using eq 11.[14a] The initial concentration of oxidant is $(A_n^+)_0$ and the initial concentration of reductant is $(A_nH)_0$. Subscripts refer to the time of measurement.

$$k_{nn}[(A_n^+)_0 + (A_nH)_0]t = -\ln(1 - F_t) \tag{11}$$

$$F_t \equiv (R_t - R_0)/(R_\infty - R_0)$$

Since the solvent contains no fluorine, reactions of fluorinated with nonfluorinated compounds could be monitored in the reaction mixtures, without extraction. Only two lines were observed in the ^{19}F NMR spectra, and all the line widths appeared to be the same, so peak heights,

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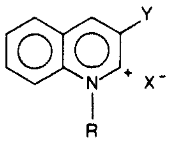
Chart II



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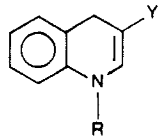
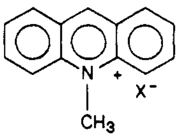


2H

compd	R	Y	X
a	CH_3	CN	I
b	$3\text{-}CF_3C_6H_4CH_2$	CN	Br
c	$4\text{-}CH_3C_6H_4CH_2$	CN	Br
d	$C_6H_5CH_2$	CN	Br
e	$4\text{-}FC_6H_4CH_2$	CN	Br
f	$4\text{-}BrC_6H_4CH_2$	CN	Br
g	$3\text{-}FC_6H_4CH_2$	CN	Br
h	$4\text{-}CNC_6H_4CH_2$	CN	Br
i	$C_6H_5CH_2$	$CONH_2$	Br
j	CH_3	$CONH_2$	I
k	$4\text{-}CNC_6H_4CH_2$	$CONH_2$	Br

Chart III



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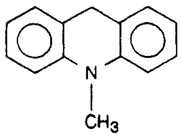
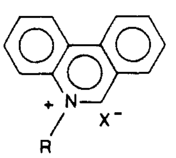


3H



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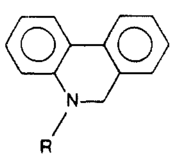

4H

compd	R	X
a	CH_3	I
b	$C_6H_5CH_2$	Br
c	$4\text{-}CF_3C_6H_4CH_2$	Br
d	$4\text{-}CNC_6H_4CH_2$	Br

rather than areas, were used as measures of species abundance. *R* was defined as the ratio of the product peak height to the sum of the two peak heights, and eq 11 was again used graphically for those reactions that had equilibrium constants of 1.0. For reaction of **2b** with **2Hh** the equilibrium constant was 1.37, so eq 12 was used.[14b]

$$k_{ij}\left(1 - \frac{1}{K_{ij}}\right)Qt = \ln \frac{R_\infty(\mathrm{A}_n{}^+)_0\{R_\infty - R_t)(\mathrm{A}_n{}^+)_0 + Q\}}{(Rf_\infty - R_t)(\mathrm{A}_n{}^+)_0\{R_\infty(\mathrm{A}_n{}^+)_0 + Q\}} \quad (12)$$

$$Q \equiv [1/(k_{ij} - 1)]\{k_{ij}[(\mathrm{A}_i{}^+)_0 - (\mathrm{A}_j\mathrm{H})_0]^2 + 4(\mathrm{A}_i{}^+)_0(\mathrm{A}_j\mathrm{H})_0K_{ij}\}^{1/2}$$

The uncertainty in *R* values, as determined by replication, when CD_3 labeling was used, was ~10%; when ^{19}F labeling was used, it was ~3%. Consistent with these values, eq 11 successfully described the observed results over about 2 half-lives of equilibration when CD_3 was used and over about 3 half-lives when ^{19}F labeling was used. There was no sign of the growth of other products, which would have been particularly obvious in the ^{19}F experiments, since these spectra contained only two lines.

Reactant concentrations ranged from 2×10^{-3} to 10^{-1} M, depending on the reactivity and solubility of the reactant. Each k_{nn} was replicated at least four times, generally using a variety of concentrations. The standard error of the average k_{nn} values ranged from 1 to 10%. The fluorine-labeling technique generally gave the better results, typically giving an average deviation from the mean of ~5% and a standard error of ~2%.

Rate constants for unsymmetrically reactions, k_{ij}, with two exceptions, were determined by standard spectrophotometric methods that have been described before.[9] In two cases a k_{ij} value was determined by monitoring the ^{19}F NMR spectrum, because the change in electronic spectrum was slight. The nonfluorinated material was used in large excess. The ratio, *R*, of the reactant ^{19}F signal to the total ^{19}F signal was taken as the fraction of unreacted reactant, and the standard first-order rate law was used to obtain a pseudo-first-order rate constant. The second-order rate constant, k_{ij}, was obtained by dividing the first-order rate constant by the concentration of the nonfluorinated reactant.

Compounds **1–4** and **1H–4H** were prepared by methods that have been previously described.[6,9,15,16] All the hydride acceptors, **1–4**, have been previously characterized[6,9,15–18] except **1e**, **1f**, **1h–k**, and **4d**.

1-Methyl-3-(*N*-benzylcarbamoyl)pyridinium iodide (**1e**): mp 136–138 °C (dec); IR (KBr) 3267 (s), 3025 (s), 1671 (vs), 1638 (s), 1540 (s), 1502 (vs), 1314 (s), 1213 (s), 1200 (m), 1151 (w), 1032 (w), 747 (s) cm^{-1}.

Anal. Calcd for $C_{14}H_{15}IN_2O$: C, 47.48; H, 4.27; N, 7.91. Found:[19] C, 47.40; H, 4.41; N, 7.97.

1-Methyl-3-(*N*-octylcarbamoyl)pyridinium iodide (**1f**): mp 117.5–118.5 °C; IR (KBr) 3332 (s), 2935 (vs), 2863 (s), 1680 (s), 1654 (vs), 1639 (s), 1549 (s), 1505 (s), 1312 (m), 826 (w), 672 (s) cm^{-1}.

Anal. Calcd for $C_{15}H_{25}IN_2O$: C, 47.88; H, 6.70; N, 7.44. Found:[19] C, 48.00; H, 6.70; N, 7.56.

1-(4-Fluorobenzyl)-3-cyanopyridinium bromide (**1h**): mp 202–205 °C (dec); IR (KBr) 3084 (m), 2937 (s), 2256 (w), 1633 (m), 1608 (s), 1505 (s), 1445 (m), 1284 (m), 1219 (vs), 1166 (m), 1138 (m), 675 (vs) cm^{-1}.

Anal. Calcd for $C_{13}H_{10}BrIN_2$: C, 53.26; H, 3.44; F, 6.48; N, 9.56. Found:[19] C, 53.09; H, 3.63; F, 6.21; N, 9.80.

1-(4-Fluorobenzyl)-3-acetylpyridinium bromide (**1i**): mp 237–239 °C (dec); IR (KBr) 3069 (m), 1698 (vs), 1609 (m), 1516 (s), 1447 (m), 1366 (m), 1229 (s), 1151 (m), 963 (m), 681 (vs) cm^{-1}.

Anal. Calcd for $C_{14}H_{13}BrFNO$: C, 54.21; H, 4.22; F, 6.13; N, 4.52. Found:[19] C, 54.38; H, 4.17; F, 6.07; N, 4.69.

1-(4-Fluorobenzyl)-3-carbomethoxypyridinium bromide (**1j**): mp 158–163 °C (dec); IR (KBr) 3081 (m), 1735 (vs), 1647 (m), 1516 (vs), 1441 (s), 1307 (vs), 1219 (vs), 1162 (vs), 993 (m), 845 (s), 742 (vs), 609 (vs) cm^{-1}.

Anal. Calcd for $C_{14}H_{13}BrFNO_2$: C, 51.55; H, 4.02; F, 5.82; N, 4.29. Found:[19] C, 51.55; H, 4.13; F, 5.90; N, 4.44.

1-(4-Fluorobenzyl)-3-carbamoylpyridinium bromide (**1k**): mp 188–191 °C (dec); IR (KBr) 3280 (vs), 3134 (vs), 1691 (vs), 1601 (s), 1507 (s), 1387 (vs), 1227 (vs), 1106 (m), 951 (w), 776 (vs), 663 (vs), cm^{-1}.

Anal. Calcd for $C_{13}H_{12}BrFN_2O$: C, 50.17; H, 3.89; N, 9.00; Br, 25.68; F, 6.11. Found:[19] C, 50.11; H, 3.94; N, 8.94; Br, 25.53; F, 6.20.

5-(4-Cyanobenzyl)phenanthridinium bromide (**4d**): mp 247–249 °C (dec); IR (KBr) 3032 (w), 2970 (w), 2237 (m), 1632 (vs), 1539 (m), 1370 (m), 1264 (m), 1159 (m), 886 (m), 763 (vs) cm^{-1}.

Anal. Calcd for $C_{21}H_{15}BrN_2$: C, 67.21; H, 4.03; N, 7.46. Found:[19] C, 67.07; H, 4.26; N, 7.54.

Among the hydride donors we have used, **1H–4H**, all are previously known and characterized[6,9,15,16,18,20] except **1He**, **1Hf**, and **1Hh**. They were prepared by the method of Mauzerall and Westheimer.[16,21] Yields were generally 50–70% after recrystallization. The compounds were stored in a refrigerator, under nitrogen. We noted no change in their original spectroscopic properties during several days or weeks of such storage.

3-(*N*-Benzylcarbamoyl)-1,4-dihydro-1-methylpyridine (**1He**): mp 86–88 °C; IR (solution in CCl_4) 3340 (w), 2933 (m), 1689 (s), 1591 (vs), 1510 (s), 1390 (m), 1260 (s), 1207 (s), 1184 (s), 999 (m) cm^{-1}.

Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.07; N, 12.27. Found:[19] C, 73.47; H, 7.11; N, 12.20.

1,4-Dihydro-1-methyl-3-(*N*-octylcarbamoyl)pyridine (**1Hf**) was a viscous liquid at room temperature which we could not crystallize. It was purified by several times dissolving it in a minimum quantity of ethanol at room temperature, filtering to remove any trace of insoluble material, and then adding water to cause the oily product to separate. IR (neat) 3342 (m), 2935 (vs), 2865 (s), 1693 (vs), 1615 (s), 1591 (vs), 1538 (vs), 1288 (vs), 1221 (s), 1124 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{26}N_2O$: C, 71.96; H, 10.47; N, 11.19. Found:[19] C, 71.70; H, 10.47; N, 11.08.

3-Cyano-1,4-dihydro-1-(4-fluorobenzyl)pyridine (**1Hh**): mp 88–90 °C; IR (solution in CCl_4) 2950 (m), 2190 (s), 1980 (vs), 1606 (vs), 1510 (vs), 1398 (s), 1220 (vs), 1169 (s), 1110 (s), 997 (m), 709 (vs) cm^{-1}.

Anal. Calcd for $C_{13}H_{11}FN_2$: C, 72.88; H, 5.17; F, 8.87; N, 13.08. Found:[19] C, 72.84; H, 5.35; F, 9.03; N, 13.03.

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Table I. Rate Constants for Symmetrical Reactions

A_n^+	$\ln K_{ij}^{\circ}$ [a]	k_{nn}, M^{-1} s^{-1}	λ_n,[b] kJ mol^{-1}
3[c,d]	0.00	4.3×10^{-2}	357
4a[c,d]	−14.56	1.8×10^{-2}	365
2i[e]	−6.19	1.6×10^{-2}	367
2a[c,d]	−0.34	2.5×10^{-3}	385
2d[d,e]	3.10	1.4×10^{-3}	391
2h[f]	4.42	1.4×10^{-3}	391
1a[e]	−11.00	1.7×10^{-4}	412
1b[e]	−15.66	8.9×10^{-4}	395
1c[e]	−17.48	7.7×10^{-4}	397
1d[d,e]	−22.00	6.5×10^{-4}	398
1e[c,d]	−26.36	3.6×10^{-3}	381

[a] K_{ij}° is the equilibrium constant for the oxidation of **3H** by A_i^+. [b] Assuming a value of −8.4 kJ mol^{-1} for W^r. [c] Measured by using CD_3 as a label for CH_3. [d] Taken from ref 10. [e] Measured by using 4-fluorobenzyl as a label for benzyl. [f] Measured by using 3-(trifluoromethyl)benzyl as a label for 4-cyanobenzyl.

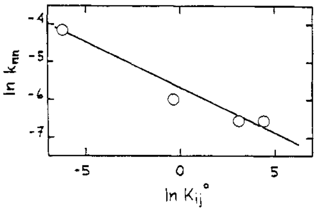

Figure 1. Relation between ln k_{nn} and ln K_{ij}° for quinoline derivatives.

In addition, we had great difficulty in crystallizing and drying 1-benzyl-3-carbomethoxy-1,4-dihydropyridine (**1Hc**) without decomposition, and our recrystallized material had mp 44–46 °C, in contrast to the 90–91 °C that has been reported.[22] (The original authors report similar difficulties, though they appear to have been more successful in overcoming them.) Nevertheless, the IR and NMR spectroscopic properties of this substance are as expected, and its long-wavelength UV absorption (λ_{max} 354 nm, log ϵ_{max} 3.86) corresponds very well with that reported:[22] λ_{max} 352 nm, log ϵ_{max} 3.86. It was, furthermore, prepared by a well-established method (dithionite reduction)[21] from a substance of well-known structure (**1c**). We are, therefore, quite confident that **1Hc** has the indicated structure.

All the substances, **1**–**4** and **1H**–**4H**, had appropriate ^1H NMR spectra.[23] For the salts, **1**–**4**, these were obtained in perdeuteriodimethyl sulfoxide. For the dihydro derivatives, **1H**–**4H**, solutions in deuteriochloroform were used. The electronic spectra of these substances were also suitable to their structures.[23]

Results

Five new rate constants for "symmetrical" exchange reactions have been measured. These are given in Table I, along with six previously reported values. Four of the new values and two of the old ones are actually rate constants for reactions of 1-(4-fluorobenzyl)-oxidizing agents with reducing agents containing an analogous 1-benzyl group. Because of dipolar and resonance effects operating in opposite directions, the Hammett σ constant for a 4-fluoro substituent is 0.062.[24] Since the ρ value for equilibria like these is 0.87 when substituents are introduced in the 1-benzyl group,[6] equilibrium constants ~1.1 were expected for such reactions. In fact, equilibrium constants evaluated from the relative magnitude of the two signals in the ^{19}F NMR spectra of equilibrated solutions were not distinguishable from 1.0. Since the 4-fluorobenzyl group is also very similar to the benzyl group in size and shape, we believe that these rate constants, within their experimental uncertainty, are identical with those for the genuinely symmetrical reactions. The same comments apply to reactions of deuteriated oxidizing agents with undeuteriated reducing agents of otherwise analogous structure; the equilibrium isotope effects should be very small.

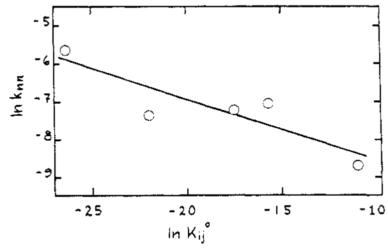

Figure 2. Relation between ln k_{nn} and ln K_{ij}° for pyridine derivatives.

Table II. Rate Constants for Symmetrical Reactions at K_{ij}° = 1.0

ring system	k_{nn}°	λ_n°
acridine	4.3×10^{-2}	357
phenanthridine	1.1×10^{-3}	392
quinoline	3.1×10^{-3}	383[a]
pyridine	2.3×10^{-5}	431[b]

[a] Obtained by applying eq 13 to the center of mass of the quinoline data. [b] Obtained by applying eq 13 to the center of mass of the pyridine data.

The reaction of **2b** with **2Hh** is less symmetrical and gave an average equilibrium constant of 1.37. Equation 2 was used to calculate a value of λ from the observed rate and equilibrium constants. This is regarded as λ_n for **2h**, though it could equally well be λ_n for **2b**. None of the subsequent development depends on this choice significantly, since K_{ij}° is very nearly the same for **2h** and **2b**.

Figures 1 and 2 show that the results are consistent with the theoretically anticipated linear relation between ln k_{nn} and ln K_{ij}°, as long as the ring system remains unchanged,[6,13] although the experimental results cannot be said to prove such a relation. The best slope for quinoline derivatives, Figure 1, is −0.24 ± 0.03 and for pyridine derivatives, Figure 2, it is −0.16 ± 0.06. (The uncertainties given are standard errors.[25]) The reference reducing agent for K_{ij}° values is 10-methylacridan (**3H**) in all cases. Since the probable errors overlap, these values are not significantly different. If the centers of mass of the two plots are superimposed, a slope of −0.19 ± 0.04 is obtained. Since this value effectively excludes a slope of zero,[25] a systematic relation of some sort, between ln k_{nn} and ln K_{ij}°, is required by the data, even in the absence of the theoretical result. Neither the data nor the theory strictly requires a linear relation. The data are too scattered to establish any form for the relation. The theory requires a linear relation only if the tightness parameter, τ, is assumed not to vary with K_{ij}°. This seems reasonable, at least as a first approximation. A linear relation has, therefore, been assumed. For the rest of this work −0.19 has been adopted as the best value of the slope. (Earlier, −0.23 had been used.[6,7])

If ln k_{nn} is a linear function of ln K_{ij}° within each structural class, with a slope of −0.19, it is possible to compare values of k_{nn} at a common value of K_{ij}°. Table II does so far K_{ij}° = 1.0. That is, the k_{nn} values are compared for the hypothetical member of each family that would have the same reduction potential as 10-methylacridinium ion, designated k_{nn}°. There is a marked dependence of k_{nn}° on the ring system involved. Although the results are limited, they suggest that the larger ring systems generate larger values of k_{nn}°. This would be consistent with the stabilization of such transition states by charge-transfer interactions between the hydride donor and hydride acceptor ring systems; the larger the ring system, the better the overlap. Such interactions, and even the spontaneous formation of complexes, have frequently been suggested for compounds such as these.[26] In view of the present and previous indications[26] of negative standard free energy of formation of such complexes, we have

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Table III. Rate Constants for Unsymmetrical Reactions

no.	oxidant	reductant	k_{ij}, M^{-1} s^{-1}	ln K_{ij}[a]
1	**3**	**4Ha**	1.12×10[b]	14.51
2	**3**	**4Hb**	4.63[c]	11.14
3	**3**	**4Hc**	1.68[d]	9.68
4	**3**	**4Hd**	1.07[d]	8.37
5	**3**	**2Ha**	2.10×10^{-2}[d]	0.34
6	**2b**	**3H**	8.59×10^{-2}[e]	4.74
7	**2c**	**3H**	3.98×10^{-2}[e]	2.75
8	**2d**	**3H**	4.51×10^{-2}[e]	3.10
9	**2e**	**3H**	4.70×10^{-2}[e]	3.27
10	**2f**	**3H**	5.67×10^{-2}[e]	3.70
11	**2g**	**3H**	6.65×10^{-2}[e]	3.83
12	**2h**	**3H**	6.91×10^{-2}[e]	4.42
13	**3**	**2Hi**	8.78×10^{-1}[c]	6.19
14	**3**	**2Hj**	6.77×10^{-1}[c]	7.70
15	**3**	**1Ha**	1.66	11.00
16	**3**	**1Hb**	1.18×10	15.66
17	**3**	**1Hc**	3.70×10	17.48
18	**3**	**1Hd**	2.14×10^{2}[c]	21.95
19	**3**	**1He**	2.83×10^{3}[f]	26.32
20	**3**	**1Hf**	1.87×10^{3}[c]	26.52
21	**3**	**1Hg**	8.28×10^{-1}	6.61
22	**4b**	**1Ha**	1.25×10^{-3}	−0.14
23	**4b**	**1Hb**	1.46×10^{-2}[d]	4.52
24	**4b**	**1Hc**	5.08×10^{-2}	6.34
25	**2i**	**1Hh**	1.31×10^{-2}[g]	4.81
26	**1h**	**1Hd**	3.83×10^{-2}[g]	10.95
27	**2j**	**4Ha**	1.62×10^{-1}[h]	6.81
28	**2i**	**4Ha**	4.24×10^{-1}[h]	8.32
29	**2k**	**4Ha**	7.35×10^{-1}[h]	10.01
30	**2c**	**4Ha**	6.95[h]	17.26
31	**2d**	**4Ha**	7.42[h]	17.61
32	**2h**	**4Ha**	9.31[h]	18.93
33	**2d**	**4Hc**	1.77	12.78
34	**2h**	**4Hc**	2.02	14.10
35	**2k**	**4Hc**	1.90×10^{-1}	5.18

[a] All obtained by making appropriate combinations of ln $K_{ij}°$ values from Table IV. [b] Previously reported[10] as 1.2×10. [c] Taken from ref 10. [d] Taken from ref 9. [e] Taken from ref 7. [f] Previously reported[10] as 3.0×10^3. [g] Determined by monitoring the ^{19}F spectra. [h] Taken from ref 27.

assumed that W^{r} (and W^{p}) is −8.4 kJ mol^{-1}, that is, that the formation of the precursor from the reactants is slightly spontaneous under standard conditions. This is a departure from our past practice.[6,10] It will be shown that the choice of W^{r} has little effect on the final comparison of calculated and observed values of k_{ij}. The values of λ_n and λ are changed when W^{r} is changed, but relative values are not. With this choice of W^{r}, it was possible to calculate λ for all the symmetrical reactions shown in Table I, using eq 2, since $\Delta G_{nn}°$ is zero. For the hypothetical reactions of Table II, λ_n values, designated $\lambda_n°$, were calculated by using eq 13, which was obtained from eq 2 and 5 and the linear relation

$$\lambda_n° = \lambda_n + 4 \times 0.19 \Delta G_{ij}°° \tag{13}$$

between ln k_{nn} and ln $K_{ij}°$. The $\Delta G_{ij}°°$ required in eq 13 is $\Delta G°$ for the reduction of the cation A_n^+ by 10-methylacridan (**3H**). Table II gives the $\lambda_n°$ values.

A total of 35 rate and equilibrium constants for unsymmetrical reactions of the type shown in eq 1 are now available. They are given in Table III. Some of these rate constants have been reported previously,[6,9,10,27] as indicated in the table, and some of those have been improved since they were first reported. None of the discrepancies is large. In all such cases we prefer the present value. Since k_{ij} and K_{ij} are both available, 35 k_{ji} can also be calculated. A number of these have also been measured independently. In cases where the measured k_{ji} was *not* used in the calculation there was typically about 10% discrepancy between the measured and calculated value. The worst discrepancy was 30%. For consistency, the K_{ij} values obtained by combining $K_{ij}°$ values were used throughout.

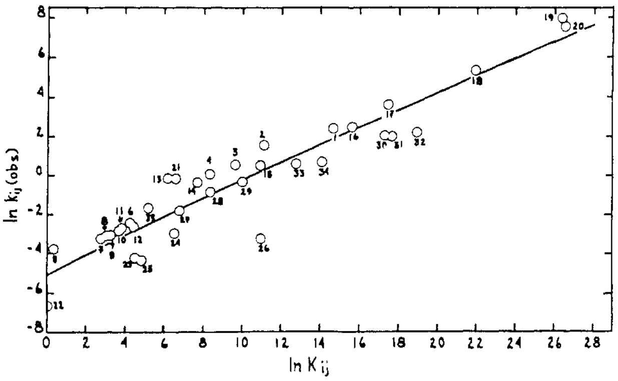

Figure 3. Relation between ln k_{ij} and ln K_{ij}. The line is the theoretical Brønsted plot (eq 2) under the assumption of a constant λ. The circles are experimental points. The numbers identify the points with entries in Table III.

If eq 2 were valid, with structure-insensitive values of W^{r} and λ, and W^{r} equal to W^{p}, then ln k_{ij} should be a smooth, slightly curved function of ln K_{ij}, given by eq 14.[11] Equations 14–16 are

$$\ln k_{ij} = a + 0.5(\ln K_{ij}) + c(\ln K_{ij})^2 \tag{14}$$

$$a = \ln (kT/h) - W^{r}/RT - \lambda/4RT \tag{15}$$

$$c = -RT/4\lambda \tag{16}$$

simply a restatement of eq 2 and 5, with the constraint that W^{r} and W^{p} are equal. This qualitative outcome was suggested long ago by Brønsted and Pedersen, and the plot is usually called a Brønsted plot.[28,29] Its slope at a particular value of K_{ij}, d(ln k_{ij})/d(ln K_{ij}), is designated α. The Brønsted plot generated by the 35 k_{ij} and K_{ij} is shown in Figure 3. Figure 3 also shows the smooth function given by eq 14–16, with −8.4 kJ mol^{-1} taken for W^{r} and 376 kJ mol^{-1} used for λ. The value for λ was arrived at by averaging the λ_n values for pyridinium ions (from Table I), averaging the λ_n values for quinolinium ions, and then taking the average of these two along with the measured values for **3** and **4a**. Although there is a recognizable correlation between the data points and the prediction of eq 14, there is a good deal of scatter. The average discrepancy between the points and the line is 0.9, corresponding to an average discrepancy of a factor of 2.5 between calculated and observed values of k_{ij}. The worst discrepancy, 3.5 log units, is for point 26, which represents a reaction between quite ordinary pyridine derivatives. It seems likely that additional discrepancies of this general magnitude would be produced if more reactions of this class were studied. The average and worst discrepancies are not appreciably changed if the suggestion of Brønsted[28,29] is followed, and the best straight line is drawn through the data points. If the 35 k_{ji} and K_{ji} were added to Figure 3, they would generate a similar Brønsted plot, to the left of $K_{ij} = 0$, showing identical discrepancies between calculated and observed ln k values. It is sobering to note that almost any value of α at all, from $+\infty$ to $-\infty$, can be obtained if one selects, arbitrarily, groups of four or more approximately collinear points and takes the best straight line through them.

Significant improvement can be achieved by taking account of the structure sensitivity of λ. For each hydride donor or acceptor λ_n was calculated by using eq 13 and the $\lambda_n°$ values given in Table II. The values of ln $K_{ij}°$ and λ_n are given in Table IV. Then, for each reaction, the appropriate λ was calculated by using eq 4. Finally, a value of ln k_{ij} was calculated, using eq 2 and 5 and the previously selected value of −8.4 kJ mol^{-1} for W^{r}. The results are shown in Figure 4. The average discrepancy between calculated and observed values of ln k_{ij} drops from 0.9 to 0.5. The largest discrepancy falls from 3.5 to 2.8. Furthermore, the most discrepant point, now point 21, corresponds to reaction of 3,5-dicarbomethoxy-1,4-dihydro-1-methylpyridine with 10-methyl-

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Table IV. Equilibrium Constants for Standard Reductions and Intrinsic Barriers for Structurally Symmetric Reactions

A_n^+	$\ln K_{ij}°$	λ_n, kJ mol^{-1}
1a	−11.00[a]	410
1b	−15.66[a]	402
1c	−17.48[a]	398
1d	−21.95[a]	390
1e	−26.32[a]	381
1f	−26.52[a]	381
1g	−6.61[b]	419
1h	−11.00[c]	410
1i	−15.66[d]	402
1j	−17.48[e]	398
1k	−21.95[f]	390
2a	−0.34[a]	382
2b	4.74[g]	392
2c	2.75[g]	388
2d	3.10[a,g]	389
2e	3.27[g,h]	389
2f	3.70[g]	390
2g	3.83[g]	390
2h	4.42[g]	391
2i	−6.19[a]	371
2j	−7.70[a]	369
2k	−4.50[b]	375
3	0.00	357
4a	−14.51[a]	365
4b	−11.14[a]	371
4c	−9.68[a]	374
4d	−8.37[a]	376

[a] Taken from ref 9. [b] Newly measured by the methods of ref 9. [c] K_{ij} of 1.0 for reaction with **1Ha**. [d] K_{ij} of 1.0 for reaction with **1Hb**. [e] K_{ij} of 1.0 for reaction with **1Hc**. [f] K_{ij} of 1.0 for reaction with **1Hd**. [g] Taken from ref 7. [h] K_{ij} of 1.0 for reaction with **2Hc**.

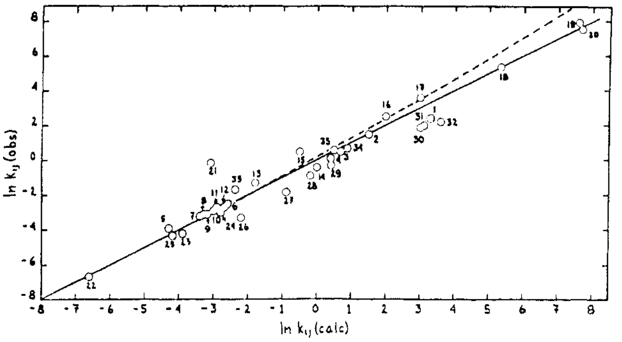

Figure 4. Relation between $\ln k_{ij}$ observed and that calculated (eq 2) using values of λ_n varying both with compound type and with $\ln K_{ij}°$, as described in the text. The solid line is the line of perfect agreement. The dashed line is a plot of $\ln k_{ij}$ (calcd) − $RT \ln (\Delta G^{\circ 2}/4\lambda)$, as the ordinate, against $\ln k_{ij}$ (calcd), as the abcissa, using a single typical value for λ, 370 kJ mol^{-1}, in the correction term.

Table V. Tests of Eq 8 and 9

data pts	$\overline{\ln K_{ij}}$	χ	tightness term[a]	cross term	α(calcd)	α(obsd)
6–12[b]	3.69	0.488	−0.095	0.000	0.39[b]	0.37 ± 0.03
15–20	19.84	0.434	+0.095	−0.002	0.53	0.47 ± 0.02
27–35	13.20	0.465	−0.095	0.001	0.36	0.39 ± 0.05

[a] ±0.5(τ − 1). [b] Previously reported in ref 6. Since then, the basis for τ has been considerably enlarged and the preferred value somewhat changed, so that the calculated value of α is somewhat changed, but the conclusions reached in ref 6 are not altered.

acridinium ion. The former is the only 3,5-disubstituted pyridine derivative in this study and $\lambda_n°$ derived from 3-substituted pyridine derivatives may not be appropriate. There is no sign of any large class of reactions generally giving discrepancies larger than about one unit. The calculated values of $\ln k_{ij}$ account for 97% of the variation in the observed values of k_{ij}. If all 70 available rate constants are considered, the theoretical values account for 99% of the variation in the experimental values.[25]

If +8.4 kJ mol^{-1} was assigned as the common value of W^{τ} and W^{p}, rather than −8.4 kJ mol^{-1}, all the λ_{nn} and $\lambda_{nn}°$ values in Tables I and II were reduced by 34 kJ mol^{-1}; however, the average change in the calculated values of $\ln k_{ij}$ was only 0.08 and the largest change (for reaction 20) was only 0.28. The average discrepancy between calculated and observed values of $\ln k_{ij}$ was unchanged.

If τ is assumed to be 1.0, $\lambda_n°$ for pyridinium ions becomes 397 kJ mol^{-1}, the average of the pyridinium values, and $\lambda_n°$ for quinolinium ions similarly becomes 384 kJ mol^{-1}. With this assumption those are the "best" λ_n values for all pyridine and quinoline derivatives, respectively. The single measured value becomes the "best" value for all phenanthridine derivatives and the experimental value is used for the 10-methylacridinium ion. With these values and −8.4 kJ mol^{-1} for W^{τ}, the $\ln k_{ij}$ values were recalculated, as before, and compared with the experimental values. The average discrepancy rises to 0.6, although the worst discrepancy drops to 1.8.

Several groups of points represent members of a family of reactions with a single value of $\lambda_n°$, which should generate smooth Brønsted plots and provide direct tests of eq 8 or 9. The results that seem reliable are summarized in Table V. These results are each based on groups of at least six points. In one case, which has been previously discussed,[6] the data were specifically collected for this purpose, and the remoteness of the structural variation from the reaction site, in the meta or para position of a benzyl group attached to nitrogen, should minimize the idiosyncratic effects.[31] In the other two cases this was not so, but the variation in $\ln K_{ij}$ is over 10 units and the slopes seem reasonably secure. In each case d($\ln k_{ij}$)/d($\ln K_{ij}$), which is the Brønsted α, was calculated for the average value of $\ln K_{ij}$ but is not expected to change significantly over the range of the data. The calculation made use of eq 8 or 9, as appropriate. The agreement between calculated and experimental values of α seems good. In two of the three cases the calculated value of α lies within the stndard error of the measured value. In the third case it is outside of those limits, but probably as good as can be expected considering the highly simplified model underlying this theory.

If the bond order of the new bond being formed by the in-flight hydrogen in the critical configuration is B_1 and the bond order to the bond being broken is B_2, then $B_1(B_1 + B_2)^{-1}$ can be regarded as a reaction progress variable, measuring the completeness of the change from a reactant-like structure to a product-like structure at the critical configuration. In the present theory $B_1(B_1 + B_2)^{-1}$ is approximately identified with the quadratic term in eq 2 and with χ.[7] Changes in α due to changes in χ are called Leffler–Hammond effects, or parallel effects.[7,32,33] Figure 4 appears to show that the removal of the quadratic term from eq 2 leads to a systematic overestimate of $\ln k_{ij}$ at large values of $\ln K_{ij}$. However, this impression is created by just three points (18, 19, and 20) and cannot be regarded as a firm conclusion. Table V shows that departures of χ from 0.5 are small in the present study, and, because of the form of eq 10, they are likely to be small for any but inherently very fast reactions. (Those will have small values of λ.) Nevertheless, the departure of χ from 0.5 is significant in two of the three cases represented in Table V, and, in all three cases, that departure improves the agreement between calculated and observed values of α.

The tightness parameter, τ, can be identified with $B_1 + B_2$.[6,7,12] Changes in α due to changes in τ are called Thornton, or perpendicular effects.[34,35] In the present work we have assumed that τ is constant. Table V shows that its departure from 1.0 has a significant effect on α, and in one case this effect is essential for the good agreement between calculated and observed values of α.

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(30) Reference 25, p 492.

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It is thought that the cross term in eq 8 and 9 will be small in most cases of interest, and Table V shows that this is true for all the present cases.

In addition to the subsets of data that have been treated in Table V, Table III contains several smaller subsets that might be treated in the same way. However, none of these subsets contains more than four points, and, in view of the difficulty of defining a homogeneous subset and the scatter, which has been commented on, it was not thought to be profitable to treat these smaller subsets.

Discussion

The improvement in correspondence between experimental and calculated points, achieved in Figure 4 by comparison with Figure 3, is mostly due to the use of a different $\lambda_n°$ value for each ring system. As shown, agreement almost as good as that of Figure 4 can be achieved by choosing $\tau = 1.0$, which makes λ_n constant for each ring system. Thus the improvement in Figure 4 over Figure 3 strongly supports the sensitivity of λ_n to the nature of the ring system, and also provides direct support for eq 4,[36] for the evaluation of λ. The overall success of the methods outlines for the calculation of λ is consistent with eq 6, 7, and 13 but does not require their correctness. However, those equations have considerable theoretical support.[6]

The value of τ to which eq 6 and 7 lead, 0.81, is intuitively reasonable. It shows a modest net loss of bonding to the in-flight hydrogen in the critical configuration. The carbon–hydrogen bonds being made and broken are probably weaker than most, and bond energies of 285–335 kJ mol^{-1} have been suggested for them.[27] The loss of 0.19 of a 315 kJ mol^{-1} bond would require ~60 kJ mol^{-1} of energy. The ΔG^* values for the reactions shown in Table III are typically ~73 kJ mol^{-1} (corresponding to k_{ij} = 1.0 M^{-1} s^{-1}). It seems entirely reasonable to assign 60 kJ mol^{-1} of this to the loss of primary binding energy, and the remainder of the various free energy requirements (nonbonded atom repulsions, the entropy requirement for making one complex out of two independently mobile entities, etc.) although such an assignment is by no means unique. The 19% excess negative charge that this treatment suggests for the in-flight hydrogen is also reasonable.[6] It is similar to previous theoretical[37] and experimental[38] estimates. In addition, the agreement between the observed values of α for the subsets and those calculated from eq 8 and 9, shown in Table V, support eq 6 and 7, since the latter are the direct precursors of eq 8 and 9. We believe that the evidence cited above provides considerable support for the reality of Thornton and Leffler–Hammond effects in this system. However, they are small, and it is far from certain that the present scheme for their quantitative evaluation, from Marcus theory, is realistic.

Part of the remaining discrepancy between calculated and observed values of k_{ij} appears to be random scatter and is probably due to individual molecular idiosyncrasies that are entirely omitted from our model. Part, however, seems systematic. For example, points 27–32, which represent a homogeneous set of reactions, all show observed values of ln k_{ij} below the calculated values by ca. one unit. Such systematic discrepancies may be due to errors in the measurements of k_{nn} or to structure specificity in W^r or remaining inadequacies in our scheme for estimation of λ. If W^r were just the free energy corresponding to the entropy decrease when two independently moving molecules are combined to make the reaction complex, it would be relatively insensitive to the structure of the reactants. But, if it contains a substantial negative contribution from a charge-transfer interactin, as now suggested, it could be sensitive both to the shapes of the reactants, because that would affect the overlap integral, and to ln K_{ij}, because that could be related to the electron-transfer energy. Experimental measurement of the equilibrium constants for complex formation between some of these reactants, or related substances, might clarify this point.

More measurements of k_{nn}, over a wider range of structural types and values of $K_{ij}°$, would also be very helpful, particularly for phenanthridinium ions, to reduce the effect of experimental errors and idiosyncracies, to test the structure invariance of τ, and to test the forms of eq 6, 7, and 13, which depend on that invariance.

The original derivation of Marcus theory of atom transfer[3] takes no specific account of either zero-point energy or tunneling. Both undoubtedly influence these hydride-transfer reactions. Some of the consequences of tunneling have been identified.[27] Marcus theory nevertheless accommodates the rate constants because these effects also accelerate the symmetric reactions, and fall off systematically as $|\Delta G°|$ increases. Thus, the effects of zero-point energy and tunneling become incorporated in the empirically determined parameters. It has been shown[27] that Marcus formalism can provide a useful framework for the understanding of rate constants even when these are quite significantly influenced by quantum effects.

It has been suggested that some reactions of the type of eq 1 are mechanistically simple hydride transfers, without high-energy intermediates, while others use a more complicated mechanism, involving first a one-electron transfer, then a proton transfer, and finally another one-electron transfer (the EPE mechanism).[39,40] Other workers appear to favor the EPE mechanism for all such reactions.[41] Equation 2, as described, is based on a model without high-energy intermediates and, of course, on the assumption that one mechanism would account for all the reactions of interest. If a multistep mechanism with high-energy intermediates were actually correct, one would expect the rate-limiting step to change over the long range of k_{ij} and K_{ij} spanned in this study. In that case one would expect the observed k_{ij} for reactions with very large K_{ij} to fall far below the calculated values, as the reaction would encounter another bottleneck, unanticipated by the theory. Figure 4 shows that this is not the case. (A recent study of kinetic isotope effects also supports the one-step mechanism and suggests that much of the evidence cited for a multistep reaction is based on artifacts.[42]) It is harder to foresee, quantitatively, the consequences of the existence of two competitive mechanistic paths, but it seems very unlikely that a theory based on a one-path model would produce the degree of correspondence between calculated and observed results that is evident in Figure 4, if the reaction actually had two paths available. We therefore conclude that the suggested mechanistic complexities are very unlikely in systems like those described in this paper.

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