

Reactivities of Five-Membered Heterocycles in Hydride Transfer Reactions

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Received April 15, 1998

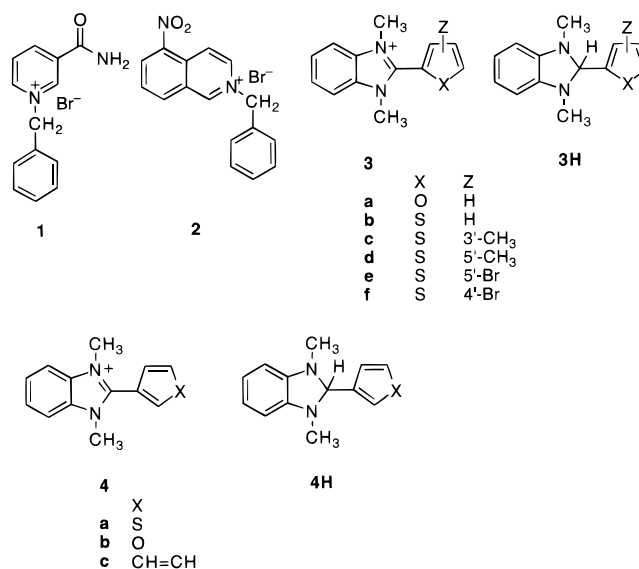
2-[2'- And 3'-furyl and thienyl]-1,3-dimethylbenzimidazoline derivatives have been prepared in order to measure the rate of oxidation of these compounds by 1-benzyl-3-carbamoylpyridinium ion and by 1-benzyl-5-nitroisoquinolinium ion. The reactions were monitored spectrophotometrically in a solvent consisting of four parts of 2-propanol and one part of water at 25 °C. The reactivities of the five-membered heterocycles fail to correlate with the acid dissociation constants, pK_a , of the corresponding heteroaromatic carboxylic acids. The variations in k_2 appear to depend more heavily on resonance involving the heteroatoms while the pK_a seems to depend mainly on the inductive effect of the heteroatoms. When rate constants for oxidation by the 1-benzyl-5-nitroisoquinolinium ion are plotted against rate constants for oxidation of the same imidazoline derivatives by 1-benzyl-3-carbamoylpyridinium ion, a linear plot with a slope of 0.96 ± 0.06 is obtained. The slope of this plot can be estimated, using Marcus theory, by taking the rates of the two calculated α values. In this way 0.95 is obtained, in good agreement with the experimental value. In this calculation it was assumed that the reactivity of isoquinolinium is about the same as that of phenanthridinium ion. These results further extend the generality of the one-step mechanism of hydride transfer, without the intervention of high-energy intermediates.

Introduction

Understanding five-membered heterocyclic compounds has been a long standing objective because they are the fundamental skeletons of more than half of the compounds produced by nature and they play important roles in biological activities.¹ The doubly unsaturated five-membered heterocycles are suitable for the Diels–Alder reaction due to the presence of conjugated double bonds in an s-cis arrangement. Yet by some criteria they are aromatic because delocalization of the π -electrons of the carbon atoms and the lone-pair electrons on the heteroatoms form a so-called aromatic 6π electron system.² Thus, there have been numerous reports of investigations of the physical and chemical characteristics of five-membered heterocycles. However, most studies were limited to a qualitative understanding of the heterocycles.³ Few reports have employed kinetic methodology to reach quantitative conclusions.⁴

We report the rate constant, k_2 , for hydride transfer reactions of 2-heteroaryl-1,3-dimethylbenzimidazoline derivatives, **3H** and **4H** (see Chart 1), with 1-benzyl-3-carbamoylpyridinium, **1**, and 2-benzyl-5-nitroisoquinolinium, **2**, ions, measured spectrophotometrically in a solvent consisting of four parts of 2-propanol and one part of water at 25 °C. There is no previous report of using 2-heteroaryl-1,3-dimethylbenzimidazolines as reducing agents for hydride transfer reactions. We have also determined the dissociation constants, pK_a , of the corresponding heteroaromatic carboxylic acids in the same

Chart 1



solvent system in order to compare the effect of the heteroaromatic group on pK_a with its effect on k_2 .

Marcus Theory

Marcus theory⁵ has been applied to hydride transfer between carbocations to demonstrate that such transfers form a single, large family of reactions.⁶ This phenomenological and approximate theory gives k_2 as a function of the reaction equilibrium constant, K , the rate constants for related degenerate reactions, and two parameters which have been previously estimated.⁶

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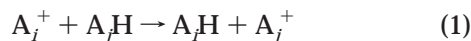
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The reactions of present interest are shown in the most general way in eq 1. Since the reactants and products



$$\Delta G^* = W^r + (1 + \Delta G^\circ/\lambda)^2 \lambda/4 \quad (2)$$

$$\lambda = (\lambda_i + \lambda_j)/2 \quad (3)$$

$$K = \exp(-\Delta G^\circ/RT) \quad (4)$$

$$k_2 = k_B T/h \exp(-\Delta G^*/RT) \quad (5)$$

are structurally related and of the same charge type, it can be assumed that the free energy required to form a reactive complex from separated reactants is the same in both directions. In that case the standard free energy of reaction, ΔG° , is the same as the standard free energy of reaction within a reactive complex, $\Delta G^{\circ\circ}$. This simplifies the Marcus theory to the form shown in eqs 2 and 3. Equations 4 and 5 give the standard thermodynamic expression for K and the quasithermodynamic expression for k_2 . The standard free energy of formation of the precursor complex from reactants, W^r , is regarded as structure insensitive. This is the standard free energy for combining the two reactants into a single unit, reducing the number of large-exursion degrees of freedom. It has been assigned a value of -8 kJ/mol,⁶ because there is thought to be a charge-transfer interaction between the reactants, and that estimation is used for the present work. As long as the assigned value is not too far from zero, it does not have an important effect on the conclusions.⁶

If ΔG° is zero, $\lambda/4 = \Delta G^* - W^r$, where $\lambda/4$ is called the intrinsic barrier, i.e., the barrier in the absence of an overall driving force. For the two degenerate reactions related to that shown in eq 1, ΔG° is necessarily zero, and $\lambda_i/4$ and $\lambda_j/4$ are the intrinsic barriers for those reactions. For a family of structurally similar hydride acceptors, such as A_i^+ , it has been shown that the variation of λ_i with the hydride acceptor tendency of A_i can be approximated by eq 6,⁶ which also defines the

$$\tau - 1 = d\lambda/d(\Delta G_i^{\circ\circ}) \quad (6)$$

parameter τ . In this equation $\Delta G_i^{\circ\circ}$ is the standard Gibbs free energy of the reaction of A_i^+ with acridan as a hydride donor. (Any other hydride donor could have been used as the standard instead of acridan, but acridan was found to be convenient.⁶) Using eq 6, the variation in rate constants of degenerate reactions with $\Delta G_i^{\circ\circ}$ can be used to evaluate the parameter τ . Or, conversely, the effect of changes in hydride affinity of A_i^+ on the value of λ_i can be evaluated from the change in $\Delta G_i^{\circ\circ}$, which is measurable. For hydride transfer between various nitrogen heterocycles, τ was found to be reasonably constant with an average value of 0.81,⁶ and this value is used in the present work. All the other symbols in eqs 2–5 have their usual significance and values.⁶

Using eqs 3–6, a Marcus theory expression for the Brønsted α [$\equiv d(\ln k)/d(\ln K)$] can be derived from eq 2 in terms of two parameters, χ and τ . It is shown in eq 7.

$$\alpha = \chi \pm 1/2\{(\tau - 1) \mp [(RT/\lambda) \ln K]^2(\tau - 1)\} \quad (7)$$

$$\chi = 1/2[1 - (RT/\lambda) \ln K] \quad (8)$$

The first term on the right-hand side of eq 7 can be defined as the parallel effect, or Leffler–Hammond effect,⁷ and the second term is the perpendicular effect, or Thornton effect on α .⁸ The third term is negligible in most applications because $(RT/\lambda)^2$ will usually be very small. It has been shown that both of the first two terms in eq 7 are required for a satisfactory estimate of α .^{6,15} The upper signs are used in eq 7 if the structural variation is in the acceptor, and the lower signs are used if the structural variation is in the donor.⁹ The present system has the structural variation in the hydride donor so we used the lower signs consistently.

τ is related to the sum of the bond orders of the in-flight hydrogen at the critical configuration. Theoretical work¹⁰ suggests that it is approximately constant over a long range of K values, as long as the end atoms are unchanged. Approximate midpoint λ and K values could be measured or estimated for each of the two reaction systems. From these α_{Py^+} , α_{IQ^+} , and their ratio could be calculated for comparison with the experimental value.

The ratio of the Brønsted α for the two systems Py^+ , **1**, and IQ^+ , **2**, can be written as shown in eq 9.

$$\alpha_{IQ^+}/\alpha_{Py^+} = [d(\ln k_{IQ^+})/d(\ln k_{Py^+})] / [d(\ln K_{IQ^+})/d(\ln K_{Py^+})] \quad (9)$$

The numerator in eq 9, the derivative involving rate constants, is accessible experimentally by measuring the rate constants, k_2 , for the two reaction systems, and the derivative involving equilibrium constants is unity for the present system because the same hydride donors, **3H** and **4H**, are used with each of the two acceptors. Since the rate constants are measured with greater accuracy than the equilibrium constants, the ratio of α values is known more accurately than the individual values. This is useful in comparing the experimental results with Marcus theory.

Experimental Section

Heteroaromatic carboxylic acids were purchased from Aldrich Chemical Co. They were used as supplied. 2-Propanol was purchased from Fisher Scientific, HPLC grade, 99.9% assay, and distilled before use. Water was also redistilled before use. The mixed solvent was made up from 2-propanol and water in a 4:1 ratio, by volume, at a temperature of 25 ± 0.1 °C.

Compounds **1**, **2**, and their dihydro derivatives, **1H** and **2H**, are previously known compounds. Their melting points and spectroscopic properties agreed with those previously reported.¹¹ Compounds **3a,b** and **4a–c** have been previously described.¹² The compounds **3c–f** were prepared similarly to **3a,b** and **4a–c** by the modification of the procedure of Craig et al.¹³ as shown in Scheme 1.

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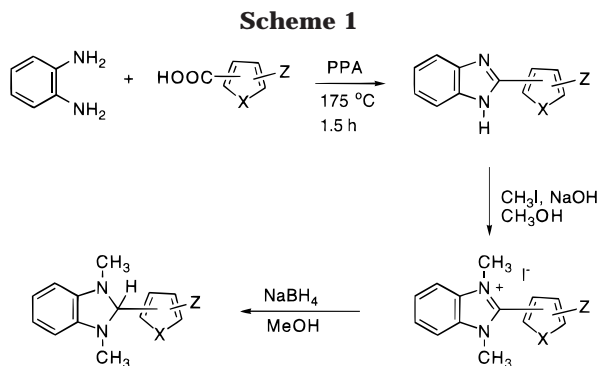
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(15) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997**, *119*, 2722–2728.



Illustrative Procedure for the Preparation of 3 and 4. An equimolar mixture of *o*-phenylenediamine, heteroaromatic carboxylic acid, and polyphosphoric acid (PPA) was stirred in an oil bath at 175–180 °C for 1.5 h. The reaction mixture was cooled to room temperature and neutralized with a 6% NH_4OH solution. The solid was filtered out, rinsed with the NH_4OH solution thoroughly, and dried to give benzimidazole derivatives (over 40% yields). The structures of the products were characterized by instrumental analyses. The benzimidazole derivatives were heated with an excess of CH_3I in methanol containing an equivalent molar amount of NaOH in a pressure tube overnight at 110 °C. The crude products, **3** and **4**, were recrystallized from aqueous ethanol ($\text{EtOH}-\text{H}_2\text{O}$, 5:1 v/v) to give products in over 70% yields.

Illustrative Procedure for the Preparation of 3H and 4H. **3** and **4** were reduced by an excess of NaBH_4 in methanol under N_2 . The reaction took place instantaneously. After reaction the solvent was removed under the reduced pressure and the product was washed with water. The products, **3H** and **4H**, were recrystallized from ethanol–water (2:1 v/v) to give a colorless crystalline product. The yield was at least 30% in all cases.

1,3-Dimethyl-2-(3'-methyl-2'-thienyl)benzimidazoline (3Hc): mp 102–103 °C; IR (KBr) 2960 w, 1490 vs, 1345 s, 1290 m, 1120 s, 730 s cm^{-1} ; UV ($\text{PrOH}-\text{H}_2\text{O}$, 4:1 v/v) λ_{max} (log ϵ) 310 (3.83), 223 (4.53); mass, m/z (%) 244 (59), 243 (93), 147 (100).

1,3-Dimethyl-2-(5'-methyl-2'-thienyl)benzimidazoline (3Hd): mp 103–105 °C; IR (KBr) 2960 w, 1495 vs, 1375 s, 1290 s, 1310 s, 730 s cm^{-1} ; UV ($\text{PrOH}-\text{H}_2\text{O}$, 4:1 v/v) λ_{max} (log ϵ) 310 (3.88), 222 (4.56); mass, m/z (%) 246 (6), 244 (100), 243 (65).

2-(5'-Bromo-2'-thienyl)-1,3-dimethylbenzimidazoline (3He): mp 125 °C; IR (KBr) 2950 w, 1600 m, 1490 vs, 1445 s, 1300 s, 1115 s, 730 s cm^{-1} ; UV ($\text{PrOH}-\text{H}_2\text{O}$, 4:1 v/v) λ_{max} (log ϵ) 309 (4.03), 241 (4.35); mass, m/z (%) 310 ($M + 2$, 22), 308 (M , 21), 147 (100).

2-(4'-Bromo-2'-thienyl)-1,3-dimethylbenzimidazoline (3Hf): mp 127–128 °C; IR (KBr) 3100 w, 1600 m, 1490 vs, 1120 s, 735 vs, 700 m cm^{-1} ; UV ($\text{PrOH}-\text{H}_2\text{O}$, 4:1 v/v) λ_{max} (log ϵ) 309 (3.89), 221 (4.68); mass, m/z (%) 310 ($M + 2$, 10), 308 (M , 10), 147 (100).

Measurements. All rate constants were measured spectrophotometrically in the 4:1 mixture of 2-propanol and water at 25 ± 0.1 °C. The kinetic measurement was conducted at 360 nm for the reaction of **1** with **4Hc**, to monitor the growth of **1H**, as shown in Figure 1, and at 480 nm for the reaction of **2** with **4Hc**, to monitor the growth of **2H**, as shown in Figure 2. Reactions were carried out with at least a 50-fold excess of the oxidizing agent in order to obtain pseudo-first-order rate constants, k_1 , shown in eq 10.¹⁴ The second-order rate

$$k_1 = t^{-1} \ln[(A_0 - A_\infty)/(A_t - A_\infty)] \quad (10)$$

constant, k_2 , was obtained by dividing k_1 by the concentration of the oxidizing agent. The measurement of the pK_a values of the heteroaromatic carboxylic acids (i.e. 2-furoic acid, 2-thiophenecarboxylic acid, etc.) was conducted electrometrically by use of a potentiometer (Metrohm 686) with a NaOH solution

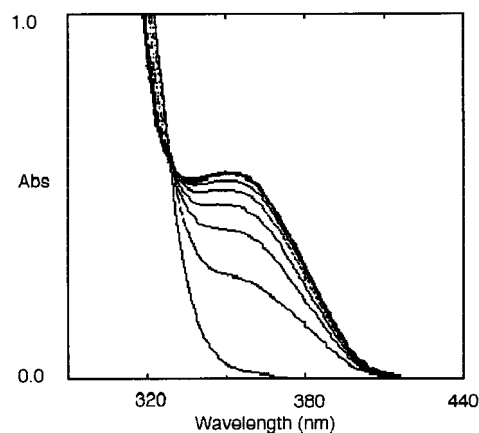


Figure 1. Absorbance as a function of time (110 min intervals) for the reaction of Py^+ (5×10^{-3} M) with **4cH** (8×10^{-5} M).

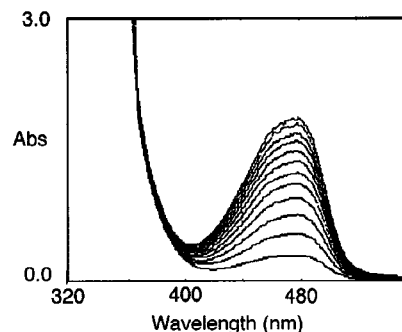


Figure 2. Absorbance as a function of time (40 s intervals) for the reaction of IQ^+ (5×10^{-3} M) with **4cH** (1×10^{-4} M).

Table 1. Spectral Data for 2- and 3-Heteroaryl-1,3-dimethylbenzimidazoline Derivatives (3H and 4H)

compd	$\delta(2\text{-H})$ (DMSO- d_6)	$\nu(\text{C-H})$, cm^{-1} (KBr)	λ , nm (log ϵ) ^a
3Ha	5.05	1490	310 (3.87)
3Hb	5.14	1490	310 (3.72)
3Hc	5.26	1490	310 (3.83)
3Hd	5.05	1495	310 (3.88)
3He	5.14	1490	309 (4.03)
3Hf	5.17	1490	309 (3.89)
4Ha	4.94	1490	311 (4.14)
4Hb	4.85	1490	309 (4.12)
4Hc	4.89	1495	312 (3.82)

^a In a mixture of 2-propanol and water (4:1, v/v).

(10^{-3} M) in the same mixed solvent. The activity coefficient, γ_{\pm} , for the present solvent system was estimated using the Debye–Huckel formula, eq 11.

$$\log \gamma_{\pm} = \frac{-1.87(I)^{1/2}}{1 + 4.05(I)^{1/2}} \quad (11)$$

A mixed solvent correction was determined by measuring the pHs of four HClO_4 solutions ranging from 10^{-2} to 10^{-4} M. The correction was made by the subtraction of 0.22 from the observed pH.

Results

The 2-heteroaryl-1,3-dimethylbenzimidazoline derivatives show common and characteristic spectral features. They are listed in Table 1. Other derivatives have similar spectral characteristics. Compounds **3** and **4** have λ_{max} around 285 nm whereas compounds **3H** and **4H** have λ_{max} around 310 nm in the 4:1 mixture of 2-propanol and water. The very strong band that ap-

Table 2. Rate Constants for Hydride Transfer Reactions

hydride donor	hydride acceptor		pK_a^a
	1 (Py ⁺) $10^3 k$ (ln k)	2 (IQ ⁺) k (ln k)	
4Ha	3.19 (-5.75)	1.51 (0.41)	6.90
4Hb	2.72 (-5.91)	1.20 (0.19)	6.73
4Hc	1.85 (-6.29)	0.95 (-0.05)	7.22
3Hd	1.49 (-6.51)		6.63
3Ha	1.38 (-6.59)	0.69 (-0.37)	5.70
3Hc	1.25 (-6.68)		7.12
3Hb	1.00 (-6.91)	0.47 (-0.76)	6.35
3He	0.81 (-7.12)		6.11
3Hf	0.28 (-8.19)		5.95

^a The pK_a of the heterocyclic carboxylic acid corresponding to the heterocycle attached to the benzimidazole.

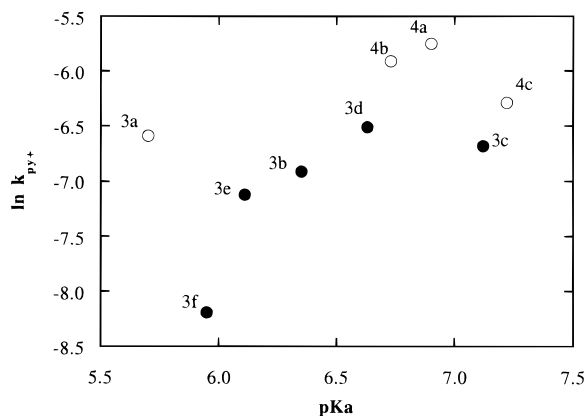


Figure 3. $\ln k$ as a function of pK_a for the reaction of **1** (Py⁺) with 2-substituted benzimidazolines. The closed circles represent reactions of 4'- and 5'-substituted and unsubstituted 2'-thienyl derivatives. Other rate constants are represented by open circles.

peaks in the IR spectra of compounds **3H** and **4H** around 1490 cm^{-1} , which is not common to other types of compounds, should be noted. This band may be due to the deformation of C2-H.

Rate constants for hydride transfer and the dissociation constants, pK_a , of the corresponding heteroaromatic carboxylic acids, are shown in Table 2. Each of the values shown is the average of at least four determinations. The average deviation from the mean of replicate values of k_2 is less than 5%. The average deviation from replicate values of mean of the pK_a is less than ± 0.01 .

A plot of k_2 for the reaction of **1** with 1,3-dimethyl-2-substituted phenylbenzimidazolines as a function of the pK_a of the corresponding benzoic acids gives a good linear correlation, as expected.¹⁵ The acid dissociation constants of five-membered heteroaromatic 2-carboxylic acids show almost the same substituent effects as benzoic acids as long as the substituent is attached to C4 or C5 in the five-membered heterocyclic ring.¹⁶ Substituents at C5 in the five-membered heterocycles are considered to behave para-like while those at C4 act meta-like. However, the plot of $\ln k_2$ for the reaction of **1** with **3H** and **4H** as a function of pK_a is very scattered, as shown in Figure 3. The situation is not much improved if only the unsubstituted compounds, **3a,b** and **4a-c**, are considered. Rate constants for hydride transfer from **3Ha,b** and **4Ha-c** to **2** similarly fail to correlate with pK_a

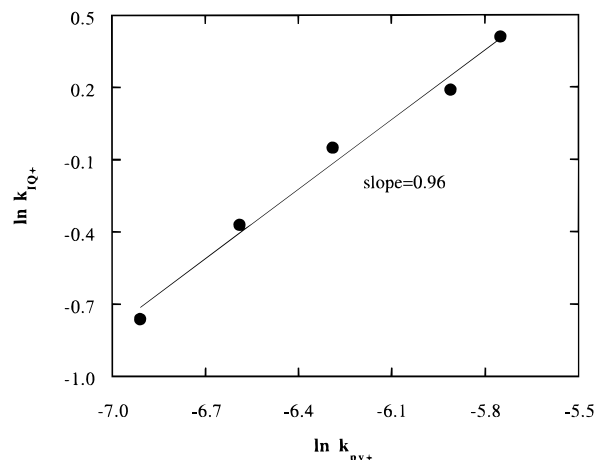


Figure 4. Correlation of rate constants with rate constants. This correlation is good, even though neither set of rate constants correlates with the K_a values of the corresponding acids. The theoretical slope, given by the ratio of calculated α values, is 0.95.

values. If only reactions of the 2-thienyl compounds, **3Hb** and **3Hd-f**, with **1** are considered (excluding the ortho-substituted **3Hc**), the correlation appears better, but the number of points is small and the range of substituent types is very limited, so no firm conclusion should be drawn. However rate constants for hydride transfer to **1** do correlate with those for hydride transfer from the same donors to **2**. That correlation is shown in Figure 4. The slope of the plot is 0.96 ± 0.06 with a correlation coefficient of 0.98.

The rate constant for hydride transfer from **4Hc** to the 5-benzylphenanthridinium ion was also measured in the same solvent system. It is $1.13\text{ M}^{-1}\text{ s}^{-1}$.¹⁵

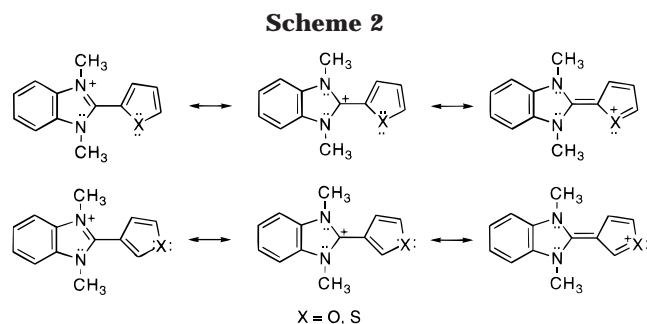
Discussion

The correlation of $\ln k_2$ with pK_a for the present system fails when it is attempted for a variety of aromatic and heteroaromatic substituents, while the phenyl compounds show a good correlation between these quantities.¹⁵ The correlation may also be acceptable for 4- and 5-substituted 2-thienyl compounds (Figure 3) although there is not enough data to be certain. For the phenyl compounds and substituted benzoic acids, the variations in both $\ln k_2$ and pK_a are mainly due to the inductive effect of the substituent. And for the heterocyclic carboxylic acids the variation in pK_a is mainly dependent on the inductive effect even though there is some involvement of the resonance effect in certain cases (e.g. pyrrole compounds). However electron delocalization by resonance is very important in the 2-substituted benzimidazolium ions, as shown in Scheme 2.

Since this resonance is absent in the 2-substituted phenylbenzimidazolium ions, the relationship between heteroatoms and the reacting site is very critical to the reactivity of the five-membered heterocycles. **3Ha** is a better hydride donor than **3Hb** even though the oxygen atom is more electronegative than the sulfur atom because oxygen is a better participant in double bonds with carbon than sulfur is.¹⁷ The main reason for the lack of correlation is the participation of the structures

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of Scheme 2 in the transition state resonance hybrid. This phenomenon has little or no influence on the pK_a values.

This kind of effect has been observed for the reaction of 1-heteroarylethyl chlorides solvolyzed in 95% acetone.¹⁸ In this reaction, 1-(2'-furyl)ethyl chloride was solvolyzed 3 times faster than 1-(2'-thienyl)ethyl chloride. The reaction was considered to take place via an S_N1 mechanism. The resonance contribution may be even more significant than in the present system, since the positive charge is probably mostly on the nitrogens in the benzimidazolium ions.

Marcus theory has previously been applied to hydride transfer among structurally related family groups. When different ring systems were introduced different λ values were required. The present system introduced not only structural variation in the substituents but also structural variation by the replacement of the heteroatoms without changing λ . (We tried to synthesize the pyrrole compounds in vain.)

The Brønsted α of the reaction of **1** with **3H** and **4H** can be calculated with the aid of Marcus theory using eq 7. The values of λ , K , and τ are required. The experimentally obtained K for the reaction of **1** with **4Hc**, **36**,¹⁵ has been chosen as representative of K values for reactions of **1** with **3H** and **4H**. λ can be obtained from eq 2 since values are available for k and K , and a constant value of -8 kJ/mol has been adopted for W^{\ddagger} ,⁶ as noted above. For the reaction with compound **4Hc**, λ is 406 kJ/mol. Using eq 7, a value of 0.58 for α is obtained.

While the equilibrium constant for the reaction of **2** with **4Hc** is not available because the reverse reaction is too slow to be measured, it has been reported that the reactivity of 2-methyl-5-nitroisquinolinium ion is very similar to that of 5-methylphenanthridinium ion in 20% CH_3CN -80% H_2O .¹⁹ In addition, the rate constant for the reaction of 5-benzylphenanthridinium ion with **4Hc** is very similar to that of **2** with **4Hc** in the same solvent system.¹⁵ Thus we have assumed that the equilibrium constant for the reaction of **2** with **4Hc** is the same as that of 5-benzylphenanthridinium ion with **4Hc**, 1.78×10^6 .¹⁵ Using these values, 392 kJ/mol is obtained for λ for the reaction of **2** with **4Hc**. Thus, a value of 0.55 is obtained for α .

According to the Hammond postulate²⁰ the Brønsted α for the reaction of **1** with **3H** and **4H** is expected to be slightly less than 0.5 because the equilibrium constant is more than unity ($K = 36$ for **4Hc**; $RT \ln K \ll \lambda$). However, in the Marcus formalism the calculated value of α is 0.58. This is significantly larger than 0.5. The

increment, 0.08, comes from the term $(\tau - 1)/2$ in eq 7. This term represents the perpendicular effect on α . The Brønsted α is not a simple indicator of the relative resemblance of the critical configuration to reactants or products (Hammond effect) but is also influenced by the resemblance of the transition state to other structures (Thornton effect).^{21,22} The present system has the structural change in the hydride donor, and consequently, the tightness factor in eq 7, which measures the importance of the nonbonded structure in which both end groups are positive and hydrogen has a negative charge, will add to the Brønsted α to give a value greater than 0.5. Since the two reaction systems have the same structural variation in the hydride donors, the effect of the tightness factor on the two α values will be the same. The difference between the two Brønsted α 's depends almost entirely on the Hammond effects. The equilibrium constant for the reaction of **2** with **3H** and **4H** is much greater than unity (10^6), so this reaction is expected to have a smaller value for the Hammond effect than that of **1**. This expectation can be realized by plotting the rate constants for **2** as a function of the rate constants for **1** as shown in Figure 4. A slope of 0.96 ± 0.06 is obtained. This value is more reliable than the Brønsted α values because it avoids the use of the equilibrium constants, which are less reliable than the rate constants.

A slope of 0.95 can be calculated for this plot by taking the ratio of the two α values given by eq 7. This calculated value is also more reliable than the individual values of α , because the ratio can be represented as $(1 + a)(1 + b)^{-1}$. Since a and b are both small, $(1 + a - b)$ is a good approximation of $(1 + a)(1 + b)^{-1}$. If we use this approximation and note that the third term in eq 7 is very small, the ratio of α values is just the ratio of χ values, to a very good approximation. Thus any uncertainty in τ does not affect the ratio of α values. The calculated ratio is in very good agreement with the experimental value. The present system is further experimental evidence for the effectiveness of the Marcus formalism, which incorporates both parallel (Leffler-Hammond) effect and perpendicular (Thornton) effect, correlating rates of hydride transfer.^{6,15} Since the Marcus formalism is based on a one-step model of the reaction, high-energy intermediates can be excluded. The reaction is a one-step hydride transfer, as previously concluded by ourselves⁶ and others.^{21,23}

Acknowledgment. We thank Professor Maurice M. Kreevoy and Dr. Ann Kotchevar for valuable discussion and proofreading the manuscript. This research was supported by the Basic Science Research Program of the Ministry of Education of the Republic of Korea (Grant BSRI-96-3401).

Supporting Information Available: ¹H NMR spectral data for of the benzimidazolines **3Hc-f** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980707S

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