

Kinetic Study of the Proton-Transfer Reactions Involving Kryptopyrrole and Its Cation in Aqueous Solution. Transition-State Structure Determinations

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Abstract: The rates of protonation (k_1^{AH}) of kryptopyrrole (**1**), i.e., 2,4-dimethyl-3-ethylpyrrole, by a variety of acids and of deprotonation ($k_{-1}^{\text{A}^-}$) of the resulting carbocation (**1**,H⁺) by the conjugated bases have been directly measured by stopped-flow spectrophotometry in aqueous solution. On the basis of protonation rates by various carboxylic acid catalysts, a Brønsted α_{AH} value of 0.54 is determined. On the other hand, the ratio $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ of the protonation rates by the solvated proton in water and deuterium oxide is equal to 2.77. Both of these results are consistent with similar data obtained in hydrogen-exchange experiments on various aromatics and with a proton transfer being about half-complete in the transition state. A significant result, however, is that an analysis of the effect of the pyrrole basicity on the protonation rates provides a similar picture of the transition state when the protonating agent is a weak acid like H_2PO_4^- but not when the protonating agent is H_3O^+ . The Brønsted β values measuring the sensitivity of the k_1^{AH} values to the changes in the pyrrole basicity are equal to 0.63 and 0.21 for H_2PO_4^- and H_3O^+ , respectively. The latter value for H_3O^+ suggests that the proton transfer has not made very much progress in the corresponding transition state. Strong support for this view is provided by the observation of large negative entropies of activation for the protonation of **1** by H_3O^+ and deprotonation of **1**,H⁺ by the solvent: $\Delta S_1^{\ddagger}(\text{H}_3\text{O}^+) = -44.8 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta S_{-1}^{\ddagger}(\text{H}_2\text{O}) = -116.80 \text{ J mol}^{-1} \text{ K}^{-1}$. It may be that these results simply reflect a general dependence of the structure of the transition state of the protonation reaction of **1** upon the nature of the catalyst or, more specifically, that solvent lag occurs in the only case of the protonation reaction by H_3O^+ . The data also permit us to estimate a Marcus intrinsic barrier for the protonation of **1**: $\Delta G_0^\ddagger = 62.9 \text{ kJ mol}^{-1}$.

Because the lone pair of electrons on their nitrogen atom is an integral part of the π -electron system, pyrrole and indole derivatives have a very low nitrogen basicity.²⁻⁶ From a determination of the basicity of carbazoles whose protonation occurs unambiguously on nitrogen, Kresge et al. have estimated a $\text{p}K_{\text{a}}$ value in the vicinity of -10 for unsubstituted nitrogen-protonated pyrrole and indole.^{2c} Accordingly, pyrroles and indoles behave preferentially as carbon bases, undergoing protonation on the α - and/or β -carbon atoms in strongly acidic solution.²⁻⁶ Thermodynamic $\text{p}K_{\text{a}}$ values for the C protonation of a number of these derivatives have been determined in aqueous sulfuric or perchloric acid solutions. While unsubstituted pyrrole and indole have $\text{p}K_{\text{a}}$ values of -3.8 and -3.62, respectively,² the presence of electron-donating group(s) appreciably increases the C basicity. Thus, a number of dialkyl and trialkylpyrroles have $\text{p}K_{\text{a}}$'s ≥ 1 in aqueous solution.^{2d}

Because they are accompanied by strong structural and solvent reorganization, protonation and deprotonation processes at a carbon atom generally occur at much lower rates than similar processes at nitrogen or oxygen atoms and are often accessible to standard kinetic techniques.⁷⁻⁹ In this context, it remains a feature of pyrrole and indole chemistry that no *direct* study of proton transfer to or from the parent molecules or their derivatives

has been reported so far.^{4,5} Although valuable information on C-protonation rates of these rings has been derived from studies of isotopic C-H exchange at low acidities,¹⁰⁻¹⁴ one could expect

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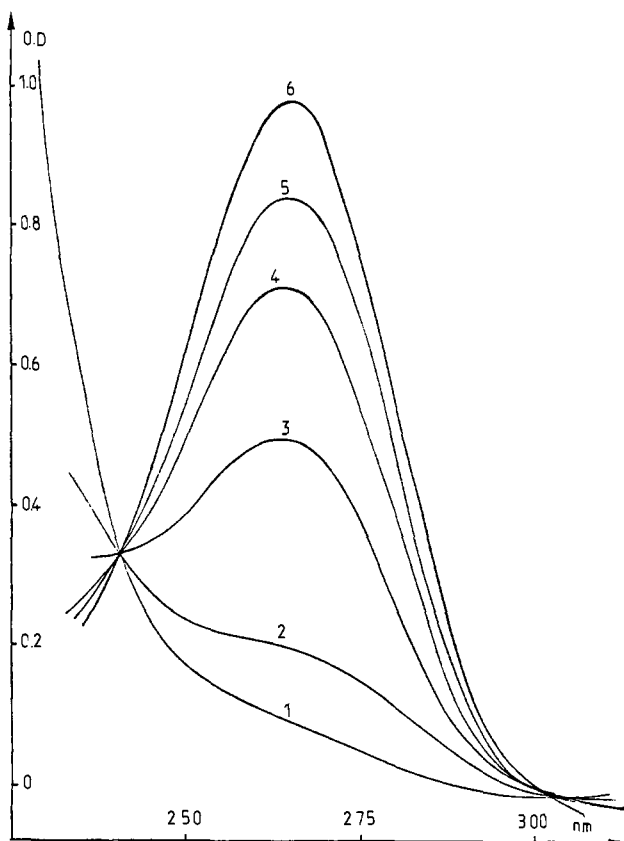


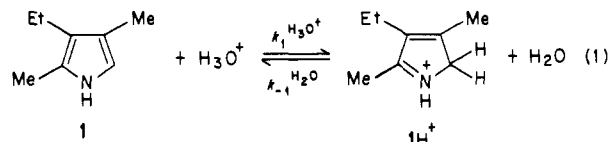
Figure 1. Ultraviolet absorption spectra of 1×10^{-4} M solutions of **1** in (1) water, (2) pH 4.18, acetic acid buffer, (3) pH 3.66, formic acid buffer, (4) pH 3.18, formic acid buffer, (5) 2×10^{-3} M HCl, and (6) 0.1 M HCl.

that a direct kinetic study of the equilibrium protonation of some pyrrole and indole derivatives would provide much interesting information on the process. In looking at the behavior of some of the most basic of these derivatives, we have found that kryptopyrrole, i.e., 2,4-dimethyl-3-ethylpyrrole, was a suitable compound for such a study in aqueous solution. The data obtained add to the understanding of electrophilic addition to these heterocycles.

Results

Protonation of kryptopyrrole **1** is known to occur exclusively at the unsubstituted C- α position to give the cation **1,H⁺** according to eq 1.^{2,3,6}

The pH dependence of the equilibrium **1** has been spectrophotometrically studied using dilute HCl solutions as well as



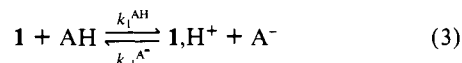
various methoxyacetic, formic, and acetic acid buffer solutions. The spectral changes are reversible, and there is a good isobestic point at 240 nm (Figure 1). From the variations at 260 nm of the optical density obtained at the equilibrium as a function of pH, a pK_a value of 3.75 was determined at 25 °C ($I = 0.1$ M KCl). Interestingly, the acidity of **1,H⁺** is essentially temperature independent; measurements at 15 and 35 °C led to pK_a values of 3.78 and 3.76, respectively.

Reaction 1 was kinetically studied at 25 °C in a stopped-flow apparatus. All experiments were carried out under pseudo-first-order conditions in aqueous solutions at $I = 0.1$ M (KCl) by monitoring the appearance or disappearance of the absorption of **1,H⁺** at 270 nm. At $\text{pH} < pK_a^{1,H^+}$, equilibrium **1** was approached from left to right by mixing an aqueous solution of **1** (about 2×10^{-4} M) with HCl solutions or appropriate buffer solutions, i.e., cyanoacetic, chloroacetic, methoxyacetic, and formic acid buffers. At $\text{pH} > pK_a^{1,H^+}$, equilibrium **1** was approached from right to left from pH-jump experiments. These were carried out by mixing a 0.01 M HCl solution of **1,H⁺** with methoxyacetic, formic, acetic, succinic, cacodylic, and dihydrogen phosphate buffers made up so as to have the desired final pH. In the buffers where eq 1 could be approached from both reactant and product sides, the rate data obtained in the two series of experiments were similar within experimental error. A strong catalysis of the reactions was observed and studied in detail. Typically, experiments were conducted at three different buffer ratios with k_{obsd} being determined at any given pH at six to eight different buffer concentrations. Most of the results have been summarized in Table S1.⁴⁰

The observed first-order rate constant k_{obsd} , reflecting the rate of approach to eq 1, is given by

$$k_{\text{obsd}} = k_{-1} \text{H}_2\text{O} + k_1 \text{H}_3\text{O}^+ [\text{H}_3\text{O}^+] + k_1^{\text{AH}} [\text{AH}] + k_{-1}^{\text{A}^-} [\text{A}^-] \quad (2)$$

While $k_1 \text{H}_3\text{O}^+$ and $k_{-1} \text{H}_2\text{O}$ are the rate constants defined by eq 1, k_1^{AH} and $k_{-1}^{\text{A}^-}$ are the rate constants referring to protonation of **1** by AH and deprotonation of **1,H⁺** by A^- , respectively, according to eq 3. The various rate constants were determined as follows.



In HCl solutions, eq 2 simplifies to

$$k_{\text{obsd}} = k_{-1} \text{H}_2\text{O} + k_1 \text{H}_3\text{O}^+ [\text{H}_3\text{O}^+] \quad (4)$$

and $k_1 \text{H}_3\text{O}^+$ and $k_{-1} \text{H}_2\text{O}$ were obtained from the slope and intercept of the plot of k_{obsd} vs. $[\text{H}_3\text{O}^+]$ which was linear.

In solutions of the two strongest buffer acids used, i.e., cyanoacetic and chloroacetic acids, the catalysis by A^- was negligible at the concentrations employed but the hydrogen ion concentration did not remain constant as the buffer concentration was varied, even at a constant buffer ratio. Such buffer failure was taken into account by calculating the hydrogen ion concentration of all buffer solutions¹⁵ and determining the k_1^{AH} values from the slopes of the $k_{\text{obsd}} - k_1 \text{H}_3\text{O}^+ [\text{H}_3\text{O}^+]$ vs. $[\text{AH}]$ plots which were linear (Figure S1).

In methoxyacetic, formic, and acetic buffers, such buffer failure was negligible but both the catalysis by A^- and AH contributed significantly to k_{obsd} . This is illustrated by Figure 2 which shows that slopes and intercepts of linear plots of k_{obsd} vs. the formic acid concentration were dependent on pH. A standard treatment of this pH dependence leads to $k_1^{\text{AH}} = 141 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}^{\text{A}^-} = 56 \text{ M}^{-1} \text{ s}^{-1}$ for methoxyacetic acid, $k_1^{\text{AH}} = 132 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}^{\text{A}^-} = 90 \text{ M}^{-1} \text{ s}^{-1}$ for formic acid and, $k_1^{\text{AH}} = 22 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{-1}^{\text{A}^-} = 196 \text{ M}^{-1} \text{ s}^{-1}$ for acetic acid. To be noted is that the corre-

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Table I. Kinetic and Thermodynamic Parameters for Protonation of Kryptopyrrole According to Equation 1 in Aqueous Solution at $t = 25\text{ }^\circ\text{C}^{a,b}$

	$t, \text{ }^\circ\text{C}$		
	15	25	35
$k_1^{\text{H}_3\text{O}^+}$, L mol ⁻¹ s ⁻¹	3155	5690	9600
$k_{-1}^{\text{H}_2\text{O}}$, s ⁻¹	0.56	1.01	1.71
K_1 , L mol ⁻¹	5635	5630	5615
pK_a	3.75, 3.78 ^c	3.75, 3.75 ^c	3.75, 3.76 ^c
ΔH_1^\ddagger , kJ mol ⁻¹		38.20	
ΔS_1^\ddagger , J mol ⁻¹ K ⁻¹		-44.8	
ΔH_{-1}^\ddagger , kJ mol ⁻¹		38.15	
ΔS_{-1}^\ddagger , J mol ⁻¹ K ⁻¹		-116.80	
ΔH_1° , kJ mol ⁻¹		0	
ΔS_1° , J mol ⁻¹ K ⁻¹		72	

^a $I = 0.1\text{ M KCl}$. ^b Estimated errors: rate constants $\pm 3\%$; ΔH^\ddagger values $\pm 1.5\text{ kJ mol}^{-1}$; ΔS^\ddagger values $\pm 5\text{ J mol}^{-1}\text{ K}^{-1}$. ^c Spectrophotometric determination.

Table II. Rate Constants for Catalysis by Buffer Species^a

N°	buffer (acid species)	pK_a^b	k_1^{AH} , L mol ⁻¹ s ⁻¹	$k_{-1}^{\text{A}^-}$, L mol ⁻¹ s ⁻¹
1	H ₃ O ⁺	-1.74	5690 ^c	0.018 ^d
2	cyanoacetic acid	2.37	418	17 ^e
3	chloroacetic acid	2.71	272	24 ^e
4	methoxyacetic acid	3.45	141	56
5	formic acid	3.60	132	90
6	acetic acid	4.64	22	196
7	succinate ion	5.60	12 ^f	850
8	cacodylic acid	6.15	21 ^f	5500
9	H ₂ PO ₄ ⁻	6.70	4.2 ^f	6000

^a $t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ M KCl}$. ^b Determined potentiometrically at $I = 0.1\text{ M KCl}$. ^c $k_1^{\text{AH}} = k_1^{\text{H}_3\text{O}^+}$. ^d $k_{-1}^{\text{H}_2\text{O}}/55.55$. ^e Calculated from k_1^{AH} via eq 5. ^f Calculated from $k_{-1}^{\text{A}^-}$ via eq 5.

spending $k_1^{\text{AH}}/k_{-1}^{\text{A}^-}$ ratios, which are equal to 2.51, 1.42, and 0.11 for the methoxyacetic, formic, and acetic acids, respectively, compared satisfactorily well with those calculated from

$$\frac{k_1^{\text{AH}}}{k_{-1}^{\text{A}^-}} = \frac{K_a^{\text{AH}}}{K_a^{\text{1,H}^+}} \quad (5)$$

which are equal to 2, 1.41, and 0.13, respectively.

For the three most basic buffers, i.e., succinic acid, cacodylic acid, and H₂PO₄⁻, the $k_{-1}^{\text{A}^-}[\text{A}^-]$ term was largely dominant in eq 2, and the slope of the k_{obsd} vs. $[\text{A}^-]$ plot provided directly $k_{-1}^{\text{A}^-}$. Then, the corresponding k_1^{AH} rate constants were calculated from eq 5. Similarly, this equation was used to estimate the rate constants $k_{-1}^{\text{A}^-}$ from the measured k_1^{AH} values for the cyanoacetic and chloroacetic acid systems.

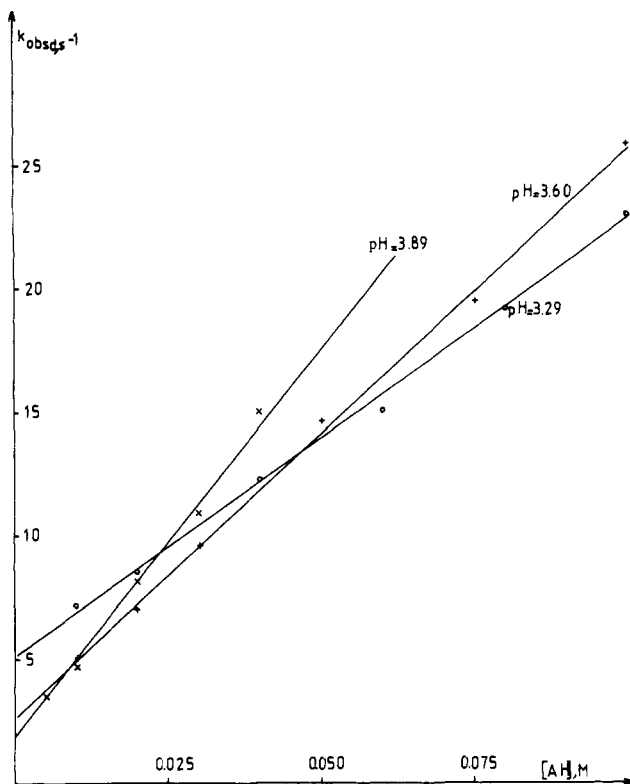
Measurements in HCl solutions were also carried out at 15 and 35 °C. The various rate and equilibrium constants for eq 1 are collected in Table I, together with the values of the corresponding activation and thermodynamic parameters. The various catalytic rate constants k_1^{AH} and $k_{-1}^{\text{A}^-}$ are summarized in Table II.

The protonation of **1** by the solvated proton was measured in DCl solutions in deuterium oxide at 25 °C. Concomitantly, that of the deuterated analogue of **1**, i.e., 5-deuterio-2,4-dimethyl-3-ethylpyrrole (**1-d**), was studied both in HCl and DCl solutions in water or deuterium oxide at 25 °C. The various $k_1^{\text{H}_3\text{O}^+}$ and $k_1^{\text{D}_3\text{O}^+}$ values thus determined, together with the evaluated isotope effects, are given in Table III.

Table III. Kinetic Hydrogen Isotope Effects on the Protonation of Kryptopyrrole^a

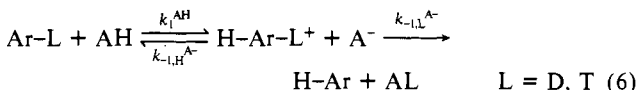
reaction	solvent		isotope effects	
	H ₂ O $k_1^{\text{H}_3\text{O}^+}$, M ⁻¹ s ⁻¹	D ₂ O $k_1^{\text{D}_3\text{O}^+}$, M ⁻¹ s ⁻¹		
1 + H ₂ O ⁺	5690		$k_1^{\text{H}_3\text{O}^+}_{(1)}/k_1^{\text{D}_3\text{O}^+}_{(1)} = 2.77$	$k_1^{\text{H}_3\text{O}^+}_{(1)}/k_1^{\text{H}_3\text{O}^+}_{(1-d)} = 1.10$
1 + D ₃ O ⁺		2055		
1-d + H ₃ O ⁺	5180		$k_1^{\text{H}_3\text{O}^+}_{(1-d)}/k_1^{\text{D}_3\text{O}^+}_{(1-d)} = 2.94$	$k_1^{\text{D}_3\text{O}^+}_{(1)}/k_1^{\text{D}_3\text{O}^+}_{(1-d)} = 1.13$
1-d + D ₃ O ⁺		1815		

^a $t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ M KCl}$.

**Figure 2.** Effect of buffer concentration and pH on the observed rate (k_{obsd}) for reaction 1 in aqueous solution; AH = formic acid; $t = 25\text{ }^\circ\text{C}$, $I = 0.1\text{ M}$.

Discussion

Inasmuch as equilibrium 1 is the first to be directly studied in the field of pyrrole or indole chemistry, there is no way for a direct comparison of the reactivity of **1** to that of related derivatives. However, acid-catalyzed aromatic hydrogen exchange in pyrroles and indoles¹⁰⁻¹⁴ as well as other basic aromatics like azulenes¹⁶ or poly(methoxybenzenes)¹⁷⁻¹⁹ is well established to proceed by the two-step reaction sequence of eq 6. Obviously, the first step



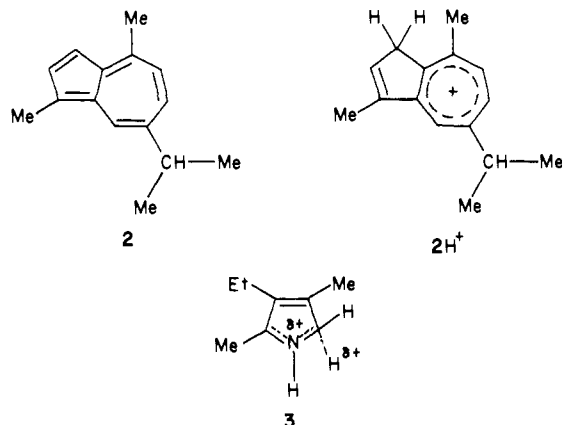
in this $\text{A}_{\text{SE}2}$ reaction mechanism is formally similar to eq 1. At the acidities employed in essentially all of the reported experiments, the protonated intermediate involved in eq 6 was present only in very low concentrations. Also, these reactions were practically nonreversible because the concentration of the generated isotopic species AL was never appreciable. Under these conditions, the observed rate law for eq 6 derived through use of the steady-state approximation is given by eq 7 where AH refers to H₃O⁺ or any general acid. Although the isotope effect $k_{1,\text{H}^+}^{\text{AH}}/k_{-1,\text{L}^+}^{\text{A}^-}$ is known

$$v = k_{\text{exch}}^{\text{AH}}[\text{AH}][\text{ArL}] = \frac{k_1^{\text{AH}}}{1 + \frac{k_{-1,\text{H}^+}^{\text{A}^-}}{k_{-1,\text{L}^+}^{\text{A}^-}}}[\text{AH}][\text{ArL}] \quad (7)$$

to vary to some extent with changes in catalyst acidity and sub-

strate basicity, the observed dependence of $k_{\text{exch}}^{\text{AH}}$ on $\text{p}K_{\text{a}}^{\text{AH}}$ for a given aromatic reflects generally that of the rate constant for protonation k_1^{AH} .^{16d,17e} Accordingly, it is of interest to relate our kinetic results for protonation of **1** according to eq 1 to those for the various exchange reactions studied according to eq 6.^{14,16-19}

Proton-Transfer Rates. Buffer Dependence. Isotope Effects. Kryptopyrrole has an appreciable C basicity, as evidenced by the measured $\text{p}K_{\text{a}}^{\text{H}_2\text{O}}$ value of 3.75 associated with eq 1 at $I = 0.1$ M, which agrees well with previously reported values of 3.50 and 3.54 at different ionic strengths.^{2,5,6} The kinetic data for eq 1 may be compared to those for the equilibrium protonation of relatively basic aromatics like azulenes.^{16d,20} The rate constant for protonation of **1** by the solvated proton is $5690 \text{ L mol}^{-1} \text{ s}^{-1}$ as compared with $k_1^{\text{H}_3\text{O}^+} = 92 \text{ L mol}^{-1} \text{ s}^{-1}$ directly determined for protonation of the most basic azulene studied, i.e., guaiazulene, **2** ($\text{p}K_{\text{a}}^{\text{H}_2\text{O}} = 1.42$).^{16c} On the other hand, the rate constant $k_{-1}^{\text{H}_2\text{O}}$



for deprotonation of the resulting conjugate acids **1,H⁺** and **2,H⁺** by the solvent are similar: $k_{-1}^{\text{H}_2\text{O}} = 1.01 \text{ s}^{-1}$ for **1,H⁺** and $k_{-1}^{\text{H}_2\text{O}} = 3.50 \text{ s}^{-1}$ for **2,H⁺** at $t = 25$ °C. Clearly, the higher stability of the pyrrolium σ complex **1,H⁺** relative to the azulonium analogue **2,H⁺** is essentially the reflection of the much higher rate of protonation of **1** than of guaiazulene, **2**.

Figure 3 shows the statistically corrected Brønsted plots for acid catalysis of the formation and base catalysis of the deprotonation of **1,H⁺**. In the case of the formation of **1,H⁺**, the points for the various carboxylic acids studied define a fairly good straight line of slope $\alpha_{\text{AH}} = 0.54$. The strong negative deviation of the point for H_3O^+ from this line is in the range of those typically observed for proton-transfer reactions on carbon atoms.²¹ Here, the deviation may in part reflect the occurrence of an electrostatic repulsive interaction between the approaching H^+ ion and the positive charge which is being developed around the nitrogen pyrrolic atom in the transition state, as visualized in **3**.²²

Available data for aromatic hydrogen exchange did not allow derivation of reliable α_{AH} values for pyrrole derivatives.¹⁰⁻¹³ However, it is noteworthy that the $k_{\text{exch}}^{\text{AH}}$ values reported for many other exchange reactions were found to fit satisfactory Brønsted relationships, with α_{AH} values being around 0.5 in all cases.^{14,16-18} For instance, α_{AH} values of 0.46, 0.59, 0.54, and 0.61 were determined for detritiation of 2-methylindole-3-*t*,¹⁴ 1,3,5-trimethoxybenzene-2-*t*,^{17d,17e} guaiazulene-3-*t*,^{16c} and azulene-1-*t*,^{16c} respectively, by homogeneous sets of carboxylic acid catalysts in aqueous solution. Clearly, such values are very similar to the α_{AH} value of 0.54 found in this work for protonation of **1**, supporting the notion that most aromatic protonation reactions involve a relatively symmetrical transition state.^{14,16,17}

The measured isotopic ratios $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ for protonation of **1** and its deuterated analogue **1-d** by the solvated proton are equal to 2.77 and 2.94, respectively. Again, these ratios which are the product of a primary isotope effect and a secondary solvent isotope effect compare well with similar data reported for aromatic-exchange reactions.^{16,17,19} Thus, $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ ratios of 2.93, 2.59, and 2.4 have been computed from $k_{\text{exch}}^{\text{H}_3\text{O}^+}$ values determined in exchange experiments on 1,3,5-trimethoxybenzene-2-*t*,^{17b,23} 2-methylindole-3-*t*,¹⁴ and azulene-1-*t*²⁰ in H_2O and D_2O solutions.

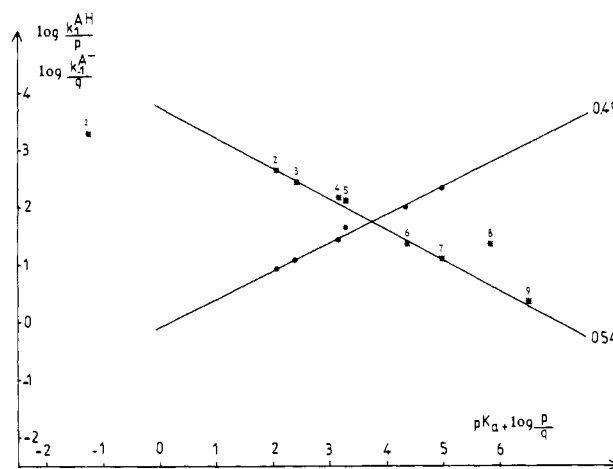


Figure 3. Statistically corrected Brønsted plots for acid catalysis of the formation and base catalysis of the deprotonation of **1,H⁺** in aqueous solution; $t = 25$ °C, $I = 0.1$ M. The numbering of the catalysts is indicated in Table II.

The fact that the $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ ratios are much lower than the analogous ratios for catalysis by any other general acid AH ($k_1^{\text{HA}}/k_1^{\text{AD}} \sim 5-7$) is a well-established phenomenon arising from an inverse secondary isotope effect of the water molecules solvating the proton:^{23,24} a maximum of ca. 3.6 has been predicted for this ratio, as compared with a maximum value of ~ 7.8 predicted for $k_1^{\text{AH}}/k_1^{\text{AD}}$.^{14,23-26} $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ ratios in the range 2.5-3 have been also found in many other $\text{AS}_{\text{E}2}$ type reactions, e.g., the hydrolysis of vinyl ethers.²⁷

To be noted is that the various $k_1^{\text{H}_3\text{O}^+}/k_1^{\text{D}_3\text{O}^+}$ ratios discussed above for aromatic protonation refer to reactions occurring at differently labeled positions (H, D, T). Hence, a rigorous comparison must take into account the secondary isotope effect arising from the changes in the nature of the isotopic substitution at the protonation site.^{17b} The data in Table III allow the calculation of these isotope effects by comparing the protonation rates of **1** and **1-d** by H_3O^+ and D_3O^+ . One thus obtains $k_1^{\text{H}_3\text{O}^+}(\text{1})/k_1^{\text{H}_3\text{O}^+}(\text{1-d}) = 1.10$ and $k_1^{\text{D}_3\text{O}^+}(\text{1-d})/k_1^{\text{D}_3\text{O}^+}(\text{1}) = 1.13$. That these isotope effects are relatively small is in accordance with general observations, but it is interesting that they are in the inverse direction to those reported by Kresge ($k_{\text{H}}/k_{\text{D}} = 0.9$; $k_{\text{H}}/k_{\text{T}} = 0.85$) for exchange experiments on 1,3,5-trimethoxybenzene.^{17b} $k_{\text{H}}/k_{\text{D}}$ ratios > 1 are not, however, uncommon in electrophilic attack on aromatic systems.^{16d,28}

That the deprotonation of **1,H⁺** is general base catalyzed was obviously to be expected based on the principle of microscopic reversibility. It is worth noting, however, that the Brønsted plot drawn through the experimentally determined $k_{-1}^{\text{A}^-}$ values for methoxyacetate, formiate, acetate, and succinate ions has a slope $\beta_{\text{A}^-} = 0.49$ which complements well the measured α_{AH} for acid catalysis of the protonation of **1**. While the slight positive deviation of the point for the HPO_4^{2-} ion may be related to the dinegative character of this catalyst,²⁹ the reason for the very large character of this catalyst,²⁹ the reason for the very large deviation of the point for cacodylate anion is less clear. Interestingly, a similar tendency of $\text{AsMe}_2\text{O}_2^-$ to be a more efficient proton-transfer catalyst than carboxylate ions of the same basicity has been recently observed by Bernasconi in a kinetic study of the reversible deprotonation of (nitrophenyl)acetoneitriles.³⁰ In this case, the possibility that part of the deviation reflects Marcus curvature has been suggested. Here the large deviation observed has to be probably understood in terms of differences in structure and/or solvation of $\text{AsMe}_2\text{O}_2^-$ and RCOO^- ions.

Effect of Pyrrole Basicity on Protonation Rates. The only results of hydrogen exchange pertaining to pyrrole derivatives which may be compared to our results for eq 1 are those reported by Butler and Alexander for protiodetritiation of the α positions of 1,3,4-trimethylpyrrole-2,5-*t*₂ (**4**) ($\text{p}K_{\text{a}}^{\text{H}_2\text{O}} = 1.4$) and the β positions of 1,2,5-trimethylpyrrole-3,4-*t*₂ (**5**) ($\text{p}K_{\text{a}}^{\text{H}_2\text{O}} \sim 0$) at 25 °C in aqueous solution.¹³ The $k_{\text{exch}}^{\text{AH}} = k_{\text{exch}}^{\text{H}_3\text{O}^+}$ and $k_{\text{exch}}^{\text{AH}} =$

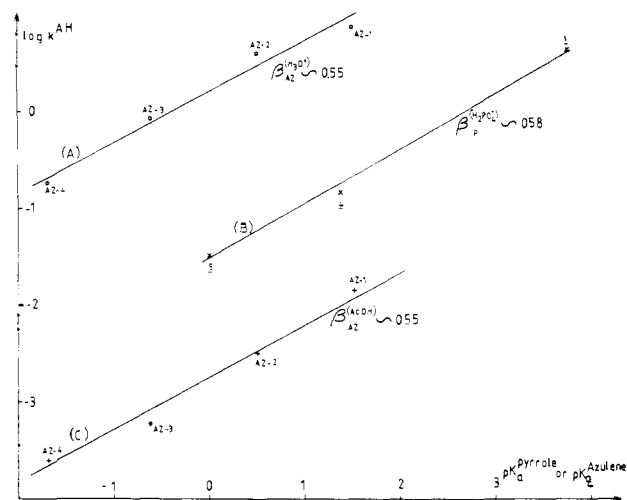
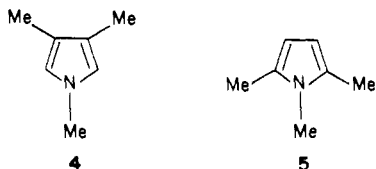


Figure 4. Brønsted relationships between protonation rates and substrate basicity in aqueous solution; plots A and C refer to the protiodetritiation rates at 25 °C of guaiazulene (Az-1 = 2), 4,6,8-trimethylazulene (Az-2), guaiazulene-2-sulfonate (Az-3), and azulene (Az-4) by H_3O^+ ($k_{\text{exch}}^{\text{H}_3\text{O}^+}$) and acetic acid ($k_{\text{exch}}^{\text{AcOH}}$), respectively.^{16c,d,17e} Plot B refers to the protonation rates at 25 °C of kryptopyrrole (1), 1,3,4-trimethylpyrrole (4), and 1,2,5-trimethylpyrrole (5) by dihydrogen phosphate ion ($k_1^{\text{H}_2\text{PO}_4^-}$).

$k_{\text{exch}}^{\text{H}_2\text{PO}_4^-}$ values for exchange by the solvated proton and dihydrogen phosphate ion are $190 \text{ L mol}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively for 4 and $200 \text{ L mol}^{-1} \text{ s}^{-1}$ and $3.3 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively, for 5 but, neither the $k_1^{\text{H}_3\text{O}^+}$ and $k_1^{\text{H}_2\text{PO}_4^-}$ values for protonation of 4 and 5 nor the isotopic ratios $k_{-1,\text{H}}/k_{-1,\text{T}}$ were determined. As noted before, the latter ratios, as well as the



analogous $k_{-1,\text{H}}/k_{-1,\text{D}}$ ratios for protiodedeuteriation, depend to some extent on the difference in the basicities of the substrate and the catalyst.^{16d,17e} However, most commonly found $k_{-1,\text{H}}/k_{-1,\text{T}}$ and $k_{-1,\text{H}}/k_{-1,\text{D}}$ ratios for hydrogen aromatic exchange are in the ranges 15–20 and 5–7, respectively, i.e., close to the observed and/or predicted maximum values for these isotope effects.^{16,17} Such observed values are in fact consistent with the median values found for the Brønsted exponents α_{AH} which imply a relatively symmetrical transition state.

If one assumes that similar relationships hold for protiodetritiation of 4 and 5, considers $k_{-1,\text{H}}/k_{-1,\text{T}} = 18$, and corrects for the statistical factor of 2 involved in Butler and Alexander's experiments, eq 7 yields the following $k_1^{\text{H}_3\text{O}^+}$ and $k_1^{\text{H}_2\text{PO}_4^-}$ values for protonation of 4 and 5: $k_1^{\text{H}_3\text{O}^+} \sim 1800 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_1^{\text{H}_2\text{PO}_4^-} = 0.133 \text{ L mol}^{-1} \text{ s}^{-1}$ for 4, $k_1^{\text{H}_3\text{O}^+} \sim 1900 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_1^{\text{H}_2\text{PO}_4^-} = 0.031 \text{ L mol}^{-1} \text{ s}^{-1}$ for 5.

Because they both refer to protonation at an α position of the pyrrole ring, let us first compare the $k_1^{\text{H}_2\text{PO}_4^-}$ value for 4 to that determined in this work for 1, i.e., 4.25 L mol^{-1} .³¹ This can be done in defining a Brønsted β_p value which will reflect the sensitivity of $k_1^{\text{H}_2\text{PO}_4^-}$ to the change in the basicity of the C- α position of the pyrrole ring. One thus obtains $\beta_p = \Delta \log k_1^{\text{H}_2\text{PO}_4^-} / \Delta \text{p}K_a^{\text{P}}$ = 0.63. This value suggests that proton transfer is about half-complete at the corresponding transition state, in accord with the picture deduced from the Brønsted α_{AH} (=0.54) value based on carboxylic acids for eq 1. In the azulene series, a similar agreement was observed between the α_{AH} values determined for protiodetritiation of azulene-1-*t* ($\alpha_{\text{AH}} = 0.61$) and guaiazulene-3-*t* ($\alpha_{\text{AH}} = 0.52$) by carboxylic acid catalysts and the β_{Az} value determined in considering the dependence of the protonation rate by acetic acid on the basicity of the azulenes (Figure 4; $\beta_{\text{Az}} \sim 0.55$).^{16c,16d,17e} Although it refers to a protonation reaction at a β position, it is

of interest that the $k_1^{\text{H}_2\text{PO}_4^-}$ value for 5 defines, together with those for 1 and 4, a satisfactory Brønsted line (Figure 4; $\beta_p \sim 0.58$). This behavior is perhaps fortuitous, but we note that a fairly good Brønsted plot (not shown) may be also obtained by plotting the reported rate constants for electrophilic attack of protonated 4-(dimethylamino)benzaldehyde to α and β positions of various pyrroles, including 5, vs. the $\text{p}K_a^{\text{P}}$ values for these derivatives.³¹

In comparing the protonation rates by the solvated proton, the situation is much less clearcut since the $k_1^{\text{H}_3\text{O}^+}$ values found for 1 and 4 do not differ very much despite the large difference in basicity of these two pyrroles. Using the same approach as before for protonation by H_2PO_4^- , one calculates a β_p value of 0.21 which suggests that proton transfer from H_3O^+ to the pyrroles has not made very much progress in the transition states for these reactions. Also, we note that the $k_1^{\text{H}_3\text{O}^+}$ values for protonation of 4 and 5 are essentially the same in contrast with the observed dependence of the corresponding $k_1^{\text{H}_2\text{PO}_4^-}$ values on the pyrrole basicity.

The above results for $k_1^{\text{H}_3\text{O}^+}$ values are somewhat unexpected in view of the excellent correspondence found between the α_{AH} and β_p values evaluated from the data obtained for protonation by the buffers. Also, all Brønsted relationships built using the results obtained in hydrogen-exchange experiments have provided convincing evidence that protonation reactions of aromatics involve relatively symmetrical transition states, including those where H^+ is the protonating agent.^{14–19} For example, the two Brønsted lines which refer to the dependence of the observed rate constants $k_{\text{exch}}^{\text{H}_3\text{O}^+}$ and $k_{\text{exch}}^{\text{AcOH}}$ for detritiation of various azulenes by H_3O^+ and acetic acid, respectively, in Figure 4 are essentially parallel with a slope $\beta_{\text{Az}} \sim 0.55$. This is consistent as mentioned above with the found median α_{AH} values ($\sim 0.56 \pm 0.05$) measuring the sensitivity of the exchange reactions of each of these azulenes to the acid strength of the catalyst.^{16c,16d} Whether our calculation of a low β_p value from the $k_1^{\text{H}_3\text{O}^+}$ rate constants indicates simply that the extent of proton transfer at the transition state of a proton-transfer reaction may depend upon the nature of the catalyst or reflects a more particular behavior of the protonation reactions of pyrroles by H_3O^+ , e.g., a transition-state imbalance,^{9,18} is therefore an interesting question. In this regard, some additional information is provided by an analysis of the activation and thermodynamic parameters related to eq 1.

As can be seen in Table I, the equilibrium protonation of 1 by the solvated proton is associated with a large positive entropy change: $\Delta S^\circ = 72 \text{ J mol}^{-1} \text{ K}^{-1}$. This result is consistent with expectations since the hydronium ion is strongly solvated in aqueous solution while protonated aromatics, i.e., σ adducts like 1, H^+ , are known to be hydrated to a much smaller extent.^{17c,20} Proton transfer from H_3O^+ to 1 must, therefore, be accompanied by liberation of some solvating water molecules, accounting for $\Delta S^\circ > 0$. Of much greater significance is the observation of an appreciable negative entropy of activation for protonation of 1: $\Delta S_1^\ddagger = -44.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Such a gain in order on going from the initial to the transition state suggests that desolvation of the proton has not made much progress in the transition state. Support for this idea is provided by the observation of an extremely large negative entropy of activation, $\Delta S_{-1}^\ddagger = -116.80 \text{ J mol}^{-1} \text{ K}^{-1}$, for the reverse reaction, which indicates that the water molecules must be already firmly bonded to the leaving hydronium ion in the transition state. Similar negative entropy changes have been observed in a number of rate-determining proton transfers which have led to the suggestion that hydronium ion desolvation cannot take place till after the actual proton transfer.³³ Such a solvent lag would not occur in the protonation of pyrroles by other general acids, accounting for the observed differences in the $\beta_p^{\text{H}_3\text{O}^+}$ and $\beta_p^{\text{H}_2\text{PO}_4^-}$ values.

While solvent lag is a common phenomenon in ionization of nitroalkanes or carbonyl compounds,^{9,18,30,34,35} its occurrence has been questioned and considered to be less likely in aromatic protonation reactions.^{17c,18} Although we will not claim that our results for eq 1 provide definitive evidence for this possibility, it is nevertheless interesting that they are consistent with such a transition-state interaction.

Intrinsic Rate Constants. An interesting feature of Figure 3 is that the two Brønsted lines intersect at a point where $\text{p}K_{\text{a}}^{\text{AH}} + \log p/q = \text{p}K_{\text{a}}^{1,\text{H}^+}$, allowing a direct determination of the "intrinsic" rate constant (in the Marcus sense) for kryptopyrrole: $\log k_{\text{o}} = 1.75$ at 25 °C in aqueous solution.³⁶ This corresponds to a relatively large intrinsic kinetic barrier, $\Delta G_{\text{o}}^{\ddagger} = 62.9 \text{ kJ mol}^{-1}$, in agreement with the fact that the reaction destroys an aromatic ring and gives an appreciably delocalized cation. Indeed, the found intrinsic barrier is comparable to those reported for ionization of carbon acids involving extensive electronic and structural reorganization.^{9,30}

From hydrogen-exchange experiments, an average value of $\Delta G_{\text{o}}^{\ddagger} \sim 80 \text{ kJ mol}^{-1}$ has been estimated for aromatic protonation.^{36,37} Using the same assumption as before, i.e., $k_{\text{H}}/k_{\text{T}} \sim 18$, more comparable $\Delta G_{\text{o}}^{\ddagger}$ values may be estimated from reported rates of deprotonation and protonation equilibrium data for azulene and 1,3,5-trimethoxybenzene.^{16,17} The $\Delta G_{\text{o}}^{\ddagger}$ values thus obtained are both of the order of 65 kJ mol^{-1} and are then comparable to that for kryptopyrrole. This shows that the intrinsic kinetic barriers for protonation of these three structurally different aromatics are very similar.

Experimental Section

Materials. 2,4-Dimethyl-3-ethylpyrrole, i.e., kryptopyrrole (**1**), was obtained commercially (Aldrich) and twice distilled under vacuum prior to use: bp¹⁵ 90–91 °C (lit. bp¹⁸ 92.5–94 °C).³⁸

Kryptopyrrole-5-*d*, i.e., **1-d**, was prepared by subjecting **1** to an acid-catalyzed exchange with D₂O, according to a procedure similar to that previously described for some indoles.¹⁵ 1 g of **1** was dissolved in a solution consisting of 3 mL of dioxane and 3 mL of DCl (1.2 M in D₂O). This solution was allowed to stand at room temperature for 3 h and then neutralized with NaOD. After filtration and removal of the solvent, the labeled pyrrole was extracted with diethyl ether. The solution was dried over MgSO₄ and evaporated to yield 1,5-dideuteriokryptopyrrole (**1-d**) which was distilled under vacuum (yield 0.78 g). The NMR resonances of the N-H (δ 9.77 ppm) and H-5 (δ 6.25 ppm) protons of **1** in

Me₂SO-*d*₆³⁹ were absent in the spectrum of **1-d**, but redissolution of this substrate in a water-dioxane mixture for a few minutes restored the NMR signal due to the NH group. Purification of the resulting product as described for **1-d**, provided a sample of **1-d** labeled at C-5 (>98% deuterium incorporation by NMR).

The kinetic experiments described in the Results section were carried out with **1-d**, but for comparison the protonation of **1-d** was also studied in HCl solutions. The kinetic results obtained with **1-d** were essentially the same as those obtained with **1** within the experimental errors.

Other materials (buffers) were all commercially available and were purified according to standard procedures.

Kinetic and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained at ± 0.3 °C. All kinetic runs were carried out in triplicate under pseudo-first-order conditions with a substrate concentration of ca. 10^{-4} M. Rate constants are accurate to $\pm 3\%$ with the exception of some $k_{-1}^{\text{A}^-}$ and k_1^{AH} rate constants which may be to $\pm 5\%$.

The pH of the buffer solutions was measured on a Tacussel Isis 20 000 electronic pH-meter according to standard methods.

Registry No. 1, 517-22-6; **1**, H⁺, 93565-19-6; **2**, 489-84-9; **4**, 30144-12-8; **5**, 930-87-0; Az-2, 941-81-1; Az-3, 93565-20-9; Az-4, 275-51-4; H₃O⁺, 13968-08-6; NCCH₂CO₂H, 372-09-8; ClCH₂CO₂H, 79-11-8; MeOCH₂CO₂H, 625-45-6; HCO₂H, 64-18-6; CH₃CO₂H, 64-19-7; HO₂C(CH₂)₂C(O)O⁻, 13479-42-0; H₂PO₄⁻, 14066-20-7; H₂O, 7732-18-5; NCCH₂C(O)O⁻, 23297-32-7; ClCH₂C(O)O⁻, 14526-03-5; MeOCH₂C(O)O⁻, 20758-58-1; HC(O)O⁻, 71-47-6; CH₃C(O)O⁻, 71-50-1; ⁻OC(O)(CH₂)₂C(O)O⁻, 56-14-4; Me₂As(O)O⁻, 15132-04-4; HPO₄²⁻, 14066-19-4; D₂, 7782-39-0; D₃O⁺, 24847-51-6; cacodylic acid, 75-60-5.

Supplementary Material Available: Observed rates of approach to equilibrium between kryptopyrrole (**1**) and its cation **1**,H⁺ in aqueous solution (Table S₁), plot of $k_{\text{obsd}} - k_1^{\text{H}_3\text{O}^+} [\text{H}_3\text{O}^+]$ vs. [AH] for the cyanoacetic buffer system with [A⁻]/[AH] = 2 (Figure S₁) (2 pages). Ordering information is given on any current masthead page.

Direct Measurement of a Prominent Outer-Sphere Electron Self-Exchange: Kinetic Parameters for the Hexaaquaruthenium(II)/(III) Couple Determined by Oxygen-17 and Ruthenium-99 NMR

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Abstract: The electron-exchange rate of the Ru(H₂O)₆^{3+/2+} couple in acidic solutions has been measured directly by ¹⁷O and ⁹⁹Ru NMR in the temperature range 252–366 K. The ¹⁷O NMR signals for the coordinated water of Ru(H₂O)₆²⁺ and Ru(H₂O)₆³⁺ occur at -200 and +35 ppm vs. H₂O and the ⁹⁹Ru signal for Ru(H₂O)₆²⁺ at +16050 ppm vs. Ru(CN)₆⁴⁻. At high temperature the electron-exchange rate is obtained from the broadening of the NMR signals of Ru(H₂O)₆²⁺ in the presence of Ru(H₂O)₆³⁺. At low temperatures the exchange is followed in the ¹⁷O NMR spectrum by a fast injection technique. At 298.15 K the rate constant k is $20 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$ and the enthalpy and entropy of activation are $\Delta H^{\ddagger} = 46.0 \pm 0.8 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -65.7 \pm 2.7 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, for a solution 2.5 M in H⁺ and 5.0 M in ionic strength, the counterion being trifluoromethanesulfonate. The effect of the acid concentration and the ionic strength is discussed. From a comparison with activation parameters calculated by using solid state properties of the hexaaqua ions, a value of ≈ 0.01 for the electronic transmission factor $\langle \kappa \rangle_{\text{el}}$ is estimated. Among the hexaaqua ions the Ru(H₂O)₆^{3+/2+} electron self-exchange represents the only unambiguous outer-sphere case since the water exchange on both hexaaqua complexes is much slower than the electron exchange.

Electron self-exchange reactions of the type



have attracted much interest as a basis for the understanding of redox reactions accompanied by a net chemical change. In spite

of the simplicity of such reactions, a direct measure is by no means simple, and only a few couples have been investigated among the hexaaqua ions, i.e., V(H₂O)₆^{3+/2+},² Cr(H₂O)₆^{3+/2+},³ Fe(H₂O)₆^{3+/2+},⁴ and Co(H₂O)₆^{3+/2+}.⁵ Information about self-ex-

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