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Marcus Theory of a Perpendicular Effect on α for Hydride Transfer between NAD$^+$ Analogues[1]

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Abstract: The Brønsted α ($\equiv d(\ln k_{ij})/d(\ln K_{ij})$) for an atom- or group-transfer reaction depends on the location of the substitution and the tightness of the transition state (τ) as well as the resemblence of the transition state to reactants and products. Within Marcus theory, τ can be related to rates of symmetrical reactions. These ideas have been successfully applied to hydride transfer between NAD$^+$ analogues. A series of 1-benzyl-3-cyanoquinolinium ions, substituted in the benzyl group, has been prepared. Rate and equilibrium constants have been determined for their reactions with 10-methylacridan. A Brønsted α of 0.37 has been obtained. From Marcus theory, using previously reported symmetrical exchange rate constants, the same value is calculated. This is displaced from 0.5 mainly by the looseness of the transition state, a perpendicular effect related to the partially hydridic character of the in-flight H. This H is estimated to have -0.23 electron of excess charge and a total bond order of 0.77 in the transition state.

In a one-step reaction of the type shown in eq 1, the Brønsted

$$A_i^+ + A_jH \rightleftharpoons A_iH + A_j^+ \quad (1)$$

α (defined as $d(\ln k_{ij})/d(\ln K_{ij})$) depends on the pattern of variation reach i and j and the charge on the in-flight H, δ, as well as K_{ij}. This occurs because structural changes that have similar effects on K_{ij} can have quite different effects on intrinsic reactivity and, consequently, on k_{ij}.[2] As an illustration, if δ is -1.0 and i is varied, then α will be 0, regardless of the value of K_{ij}. On the other hand, if j is varied, α will be 1.0. Only if δ is 0 does there appear to be a simple relation between α and K_{ij}, independent of which subscript is varied, as suggested by the Leffler–Hammond principle.[3] Using the Marcus theory of atom and group transfer,[4-6] these patterns can be used to evaluate δ and the tightness parameter, τ,[6] and to calculate α for comparison with experiment. This can be done by relating the rate constants for symmetrical reactions, k_{ii}, to the equilibrium constants, K_{ij}, obtained when the same series of oxidizing agents, A_i^+, reacts with some single reducing agent, A_jH. If δ is -1, the ratio of two k_{ii} values is the inverse of the ratio of K_{ij} values, because one A_i–H bond is broken to reach the transition state, while an identical bond is formed in the products. For similar reasons, if δ is 0, k_{ii} is invariant; if δ is $+1$, the ratio of k_{ii} values is the same as the ratio of K_{ij} values.

For the reaction of eq 1, a two-dimensional transition-state map (an Albery–More-O-Ferrall–Jencks diagram) is shown in Figure 1. If the transition state is in the upper right corner of the diagram, τ, which was defined as the sum of the orders of the reacting bonds to the atom in flight,[6] is 0, and δ is -1. If the transition state lies anywhere on the upper left-lower right diagonal, τ is 1.0 and δ is 0. If the transition state is in the lower left corner, τ is 2.0 and δ is $+1.0$. If τ is redefined by means of eq 2, it has the correct values at these three points as shown in

$$\tau - 1 = d(\ln k_{ii})/d(\ln K_{ij}) \quad (2)$$

the first paragraph and appears to behave in a way consistent with the original definition and eq 3 everywhere. The derivative is

$$\tau - 1 = \delta \quad (3)$$

an experimentally accessible quantity if rate constants for symmetrical exchange reactions, k_{ii}, can be measured. It is simply the slope of a plot of $\ln k_{ii}$ against $\ln K_{ij}$.

Within the Marcus formalism a relation between α and τ can be derived that qantifies these effects. The Marcus relations are given in eq 4–6. The symbols have their usual significance.[5] If

$$\Delta G_{ij}^* = W^r + (1 + (\Delta G_{ij}^{\circ\prime}/\lambda))^2(\lambda/4) \quad (4)$$

$$\Delta G_{ij}^{\circ\prime} = \Delta G_{ij}^\circ - W^r + W^p \quad (5)$$

$$\lambda = (\lambda_{ii} + \lambda_{jj})/2 \quad (6)$$

W^r and W^p are assumed to be small, structure insensitive, and roughly equal, then $\Delta G_{ij}^{\circ\prime}$ becomes equal to ΔG_{ij}° and can be replaced with $-RT \ln K_{ij}$; eq 4 can be rearranged into eq 7, with

$$\ln k_{ij} = a + 0.5(\ln K_{ij}) + c(\ln K_{ij})^2 \quad (7)$$

$$a = (-\lambda/4RT) - (W^r/RT) + \ln(kT/h) \quad (8)$$

$$c = -RT/(4\lambda) \quad (9)$$

the coefficients of the power series given in eq 8 and 9. If we now consider the particular case that A_i is varied and A_j is constant, then α is given by eq 10. The derivation is shown in the Appendix.

$$2\alpha = 1 - ((RT/\lambda)\ln K_{ij}) + (\tau - 1) - (RT/\lambda)^2(\tau - 1)(\ln K_{ij})^2 \quad (10)$$

This derivation takes account of the fact, implied in the first paragraphs, that λ varies in a systematic way with $\ln K_{ij}$, except in the special case that τ is 1.0. The second term on the right-hand side of eq 10 is the Leffler–Hammond contribution to α, the third is the perpendicular (Thornton[7]) contribution, and the last is a cross term, which is likely to be small in most applications because $(RT/\lambda)^2$ will usually be very small.

We now define χ as $0.5\,[1 - ((RT/\lambda)\ln K_{ij})]$. This quantity has the properties formerly ascribed to α. It is $\delta(\ln k_{ij})/\delta(\ln K_{ij})$ or $\delta(\Delta G^*)/\delta(\Delta G^\circ)$ at constant λ and measures the transition-state value of the coordinate orthogonal to τ, as shown in Figure 1. Equation 10 then simplifies to eq 11, which can be further

$$\alpha = \chi + 0.5(\tau - 1) - 0.5(RT \ln K_{ij}/\lambda)^2(\tau - 1) \quad (11)$$

simplified by dropping the last (small) term in the present case, and probably in most others.

Equation 10 has been successfully applied to the reaction shown in eq 1 with **1** as A_i^+ and **2** as A_j^+.

Experimental Section

Rate and equilibrium constants were measured in a solvent containing 4.00 parts of isopropyl alcohol to 1.00 part of water by volume at 25 °C. Compounds **1a–i**, **2**, **3a,b**, and their dihydro derivatives were all prepared by methods that have been previously described.[8] Compounds **1b**, **2**,

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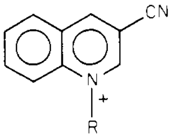
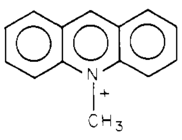


1a, R = $p\text{-}CH_3C_6H_4CH_2$
b, R = $C_6H_5CH_2$
c, R = $p\text{-}FC_6H_4CH_2$
d, R = $p\text{-}BrC_6H_4CH_2$
e, R = $m\text{-}FC_6H_4CH_2$
f, R = $p\text{-}CNC_6H_4CH_2$
g, R = $m\text{-}CF_3C_6H_4CH_2$
h, R = $p\text{-}CF_3C_6H_4CH_2$
i, R = CH_3



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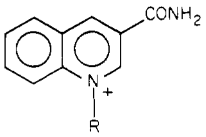


3a, R = CH_3
b, R = $CH_2C_6H_5$

3a,b, and their dihydro derivatives are previously known compounds, and their melting points and spectroscopic properties agreed with those previously reported.[8-10] For all the rest elemental analyses were obtained for C, H, N, Br, and F where appropriate. For each element in each substance the analytical result was within 0.25% of the calculated percentage. The ^1H NMR, IR, and electronic spectra of these compounds were consistent with the assigned structures.[8] In particular, the dihydro derivatives of the variants of **1** were all free of absorption in their electronic spectra at wavelengths above 420 nm and the absorption of **2** above 400 nm showed the well-known structure, with appropriate λ_{max} and ϵ_{max} values.[11]

Rates were measured spectrophotometrically. Reacting solutions were maintained in the temperature-regulated cell compartment of a spectrophotometer (thereby protected from light) for the duration of measurements. Experience suggests errors of no more than 0.2 deg in the temperature.

Values of $k_{ij}Qf$, pseudo-first-order rate constants, were obtained by application of eq 12, in the usual way, and these gave k_{ij} values. Q is the

$$k_{ij}Qf = t^{-1} \ln [(A_0 - A_\infty)/(A_t - A_\infty)] \qquad (12)$$

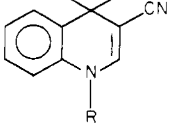
concentration of the quinolinium ion, which was the oxidizing agent in these cases, and was always in exccess by at least a factor of 20. The fraction of active (unhydroxylated) form of quinolinium ion, f, was determined as described below.

To get the equilibrium constant K_{ij}, eq 13,[12] along with an estimate

$$k_{ji}Q = \left(\frac{p_\infty}{2e - p_\infty}\right)t^{-1} \ln \left(\frac{p_t(e - p_\infty) + ep_\infty}{e(p_\infty - p_t)}\right) \qquad (13)$$

of K_{ij}, was used to obtain a first approximation of k_{ji}. In this equation, e represents the initial concentration of the limiting reactant (usually **2**) and p represents the (equal) concentrations of the two products. Unlike eq 12, eq 13 requires that actual concentrations be known. These were determined from the stoichiometry of the reaction mixture and its absorbance at 420 nm, which is entirely due to the methylacridinium ion. K_{ij} was then reevaluated at k_{ij}/k_{ji}. The cycle was repeated until consistency was achieved. Usually no more than two iterations were necessary. The quinolinium ions were found to add hydroxide of the solvent according to eq 14.[13] The equilibrium constants for this reaction, K_R, were determined from spectra of the quinolinium ions in a series of buffer solution with pH's between 3.5 and 7.5 and, in most cases, in 4 × 10^{-3} M NaOH. A typical set of spectra is shown in Figure 2. The long-wavelength absorptions of the variants of **4** are very similar to those of the dihydroquinolines. The solution pH values were determined electrometrically. The spectrum in 4 × 10^{-3} M NaOH was taken as the spectrum of **4**, and at intermediate pH's, the ratio of **4** to **1** was determined from the intensity of their characteristic absorptions around 332 and 300 nm. High-pH solutions of the two strongest pseudoacids, **1f** and

$$1 + H_2O \rightleftharpoons 4 + H^+ \qquad (14)$$



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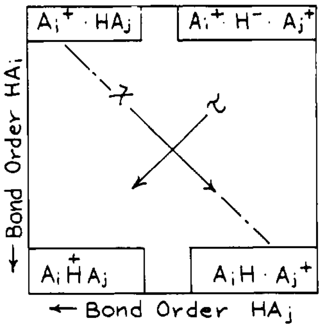

Figure 1. Two-dimensional transition state map for hydride transfer between substituted pyridinium ions (eq 1) showing the tightness parameter, τ, the total bond order of the in-flight atom. In the present case τ − 1 also gives the charge on the in-flight H. τ is 0 in the upper right corner and 2 in the lower left. Along the upper left corner right diagonal τ is 1.0. Only on that diagonal is α (≡ d(ln k_{ij})/d(ln K_{ij})) a simple measure of the resemblence of the transition state to starting state or product, and equal to χ.

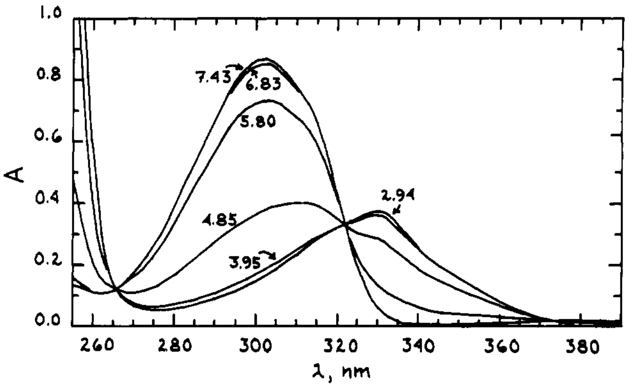

Figure 2. Spectra of 4.92 × 10^{-3} M **1b**, in a cell with a 1-mm path length, at various pH values, as shown. The spectrum in the presence of 4 × 10^{-3} M NaOH was essentially the same as that at pH 7.43. The base line was experimentally determined and was not significantly different from the line for A of 0. The absorbance ~380 nm at high pH is real and thought to be due to the presence of small amounts of 1-benzyl-2-hydroxy-1,2-dihydroquinoline, in equilibrium with **4b**.

Table I. Hydride Transfer to and Hydroxylation of Quinolinium Ions

A_i	k_{ij},[a] M^{-1} s^{-1}	K_{ij}[a,b]	10^6K_R,[a] M^{-1}
1a	3.98 × 10^{-2}	15.7	3.6
1b	4.51 × 10^{-2}	22.2	4.9
1c	4.70 × 10^{-2}	26.4	6.3
1d	5.67 × 10^{-2}	40.5	10.0
1e	6.65 × 10^{-2}	45.9	11.2
1f	6.91 × 10^{-2}	83.3	24.0
1g	8.59 × 10^{-2}	114.4	23.4
1h	7.03 × 10^{-2}	26.3	16.6
1i	8.1 × 10^{-3} [c]	3.2 × 10^{-1} [c]	*d*
3a	3.1 × 10^{-4} [c]	4.5 × 10^{-4} [c]	*d*
3b	1.8 × 10^{-3} [c]	2.0 × 10^{-3} [c]	*d*

[a] The precision and accuracy of these values is discussed in the text. [b] Dimensionless. [c] Taken from ref 17. [d] Not measured; not large enough to interfere with the determination of k_{ij} and K_{ij}.

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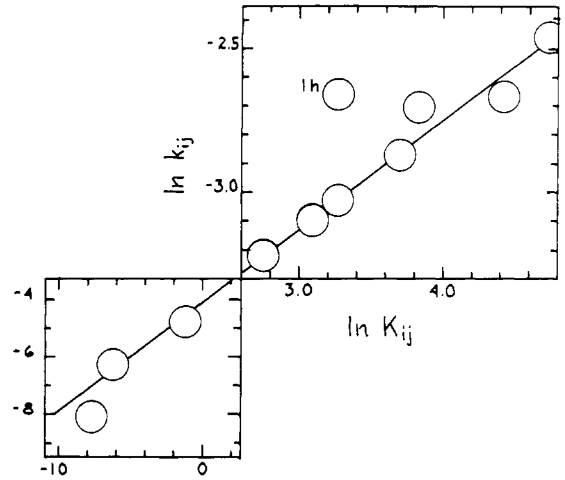

Figure 3. ln k_{ij} as a function of ln K_{ij}. The points generated by compounds **1a–h** are in the main section, upper right. The circles in this section give a rough estimate of the estimated accuracy of the data. The point for **1h**, which was not used in the correlation, is identified. In the extension to the lower left both scales are compressed by a factor of 10. This section shows the fit of the points generated by **1i** and **3a,b** to the extrapolation of the line correlating the points generated by **1a–g**.

1g, did not give spectra that were members of the families generated by lower pH solutions (pH ≤7.5). Above this pH the steady increase in absorbance around 300 nm was reversed and significant departures from the isosbestic points was observed. Fortunately, for these two compounds, the solutions at pH ~7.5 seemed to already generate the limiting spectra of **4f** and **4g**, and they were used as such. The K_R values were then obtained from eq 15, in which $\gamma_\pm$ is the activity coefficient of the al-

$$K_R = \frac{[4]10^{-pH}}{[1]\ \gamma_\pm} \qquad (15)$$

kylquinolinium ion, given by eq 16.[14,15] After K_R was known, f was given

$$\log \gamma_\pm = -\frac{1.87I^{1/2}}{1 + 4.05I^{1/2}} \qquad (16)$$

by [1]/([1] + [4]), where the concentrations were obtained from eq 15, the pH, and the known stoichiometric quinolinium ion concentration.

Results

The resulting k_{ij}, K_{ij}, and K_R values are shown in Table I. These were all measured at 25.0 °C, in a solvent consisting of 4 parts of isopropyl alcohol to 1 part of water, by volume, at 25 °C. Each of the values shown is the average of at least four determinations. For k_{ij} the average deviation from the mean is 1–2%. Past experience suggests that this scatter is mainly due to errors in temperature (an error of 0.1 deg leads to an error of ~1% in k_{ij}). There are also small uncertainties in Q and in the solvent composition, but we do not believe that any of the reported values of k_{ij} are in error by as much as 5%. The average deviation from the mean of the K_R values was not larger than 5%. We believe that this is primarily due to uncertainties in pH. These include both the reproducibility of the measurement itself (±0.02) and the reproducibility of the correction to the mixed solvent, which we estimate to be ~0.02. An error of 0.04 in pH produces an error of 10% in K_R. Other systematic errors (in concentrations and ϵ values) probably make the K_R values uncertain by ~15%. The values of k_{ji} scattered by no more than ±4%, but errors in ϵ and K_R can contribute systematically to errors in K_{ij} (though, fortunately, errors in K_R did not contribute proportionately, since f was usually >0.9). We, therefore, consider the K_{ij} value to be uncertain by ~10% when the oxidizing agent is one of the compounds **1a–h**. When the oxidizing agent is **1i**, **3a**, or **3b**, K_R is considerably smaller, and f is 1.00, so that the value of K_R does not come into question. These values of K_{ij} are probably within 5% of the true values.

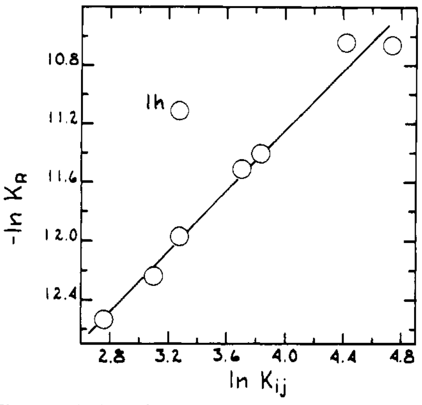

Figure 4. The correlation of ln K_R with ln K_{ij}. The deviant point for **1h** (identified) was not used in evaluating the correlation.

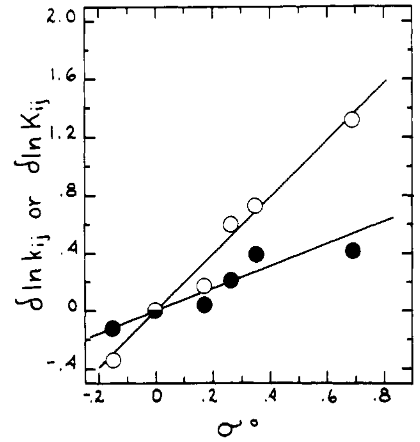

Figure 5. The correlation of ln k_{ij} (filled points) and ln K_{ij} (open points) with σ°.[16] δ indicates that the corresponding quantity for **1b**, the unsubstituted benzyl compound, has been subtracted.

It was anticipated that ln k_{ij} would be a linear function of ln K_{ij} for oxidizing agents differing only by substitution in the benzyl group.[16] This expectation was realized for compounds **1a–g**. The slope of this plot, which is α, is 0.37, with a probable error of 0.03 and a correlation coefficient of 0.98; all were determined by the method of least squares. The correlation is shown in Figure 3. Structurally, **1i**, **3a**, and **3b** are somewhat different from **1a–h**, nevertheless they generate points quite close to an extrapolation of the line defined by the points for **1a–g**, as shown in Figure 3. It was, therefore, concluded that all of these reactions may be considered part of a single, homogeneous group. There is also a good, linear correlation of ln K_R with ln K_{ij} for compounds **1a–g**, as shown in Figure 4, with slope of 1.02 and correlation coefficient of 0.99. From both of these correlations, the point generated by **1h** is strongly deviant, as shown in Figures 3 and 4. We believe that this K_{ij} is probably in error by about a factor of 2, but we have been unable to find the cause of the difficulty. The results obtained with **1h** have not been used in subsequent calculations.

For compounds **1a–f**, both ln k_{ij} and ln K_{ij} are linearly correlated with the Taft σ° parameters,[16] as shown in Figure 5, giving ρ values of 0.34 and 0.87, respectively. The slopes of the correlation lines have been divided by 2.3 to put these ρ values on the usual scale. σ° values are not available for *m*- or *p*-trifluoromethyl groups. These correlations, and the correlations of ln K_R with ln K_{ij}, tend to validate the correlation of ln k_{ij} with ln K_{ij} and the value of α derived from it.

A value of τ is available from the rate constants for near-symmetrical hydride transfer for **1b**, **1i**, and **3b**: 1.4×10^{-3} M^{-1} s^{-1}, 2.5×10^{-3} M^{-1} s^{-1}, and 1.6×10^{-2} M^{-1} s^{-1}, respectively.[17] To make measurement possible the methyl group in **1i** was replaced

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with a trideuteriomethyl group and the benzyl groups of **1b** and **3b** were replaced with *p*-fluorobenzyl groups. All the dihydro derivatives were unlabeled. The equilibrium constants were indistinguishable from unity (±5%). Rate and equilibrium constants were measured by ^{1}H NMR spectroscopy for **1i** and by ^{19}F NMR spectroscopy for **1b** and **3b**. These rate constants give a value of 0.23 for $\Delta\ln k_{ii}/\Delta\ln K_{ij}$ (assumed equal to the derivative) and 0.77 for τ. A central value of K_{ij} for **1a–g** is ~60, and λ is ~77 kcal mol^{-1},[17] so χ is 0.48. When these values are inserted in eq 11, a value of 0.37 is calculated for α, which is in fortuitously good agreement with the experimental value, 0.37. The calculated excess charge on the in-flight H, δ, is −0.23 electron.

Discussion

The credibility of results like these depends on their agreement with intuition and with results obtained in other ways. It is reasonable that the in-flight H should bear a partial negative charge in a hydride-transfer reaction. The general reluctance of H to acquire a large excess of electrons in combinations with carbon[18] makes it reasonable that this charge should be small. The magnitude of the charge deduced here is less than the value, −0.44 electron, obtained in a more empirical study of relative reactivities in a closely related series.[19] It is greater than the values, −0.006 to −0.13 electron, calculated for hydride transfer between cyclopropenium ions by a variety of approximate theoretical methods.[20] Altogether, the present value seems reasonable.

It is interesting to note that the perpendicular (Thornton) effect on α is much larger than the Leffler–Hammond effect. The former is of respectable magnitude (0.12) even though H is reluctant to acquire net charge from C. If a group less reluctant to take up charge, such as an alkyl group, is being transferred (displacement at carbon) much larger perpendicular effects can be expected.[21] This may help account for the apparently anomalous Brønsted parameters that have been observed for nucleophilic displacements on alkyl halides.[22]

A treatment identical with this has been successfully applied to methyl-transfer reactions in sulfolane solution,[23] and a similar treatment has been used for gas-phase methyl-transfer reactions.[24]

The present A$_i$ and A$_j$ were chosen to minimize the Leffler–Hammond effect, so as to emphasize the Thornton effect. In consequence, the present results do not even demonstrate the existance of the Leffler–Hammond effect. This problem will be addressed in a future publication.

The success of the present treatment adds to the evidence previously presented[17] that Marcus theory gives a reasonably accurate representation of the relation between rate and equilibrium constants for reactions of the type shown in eq 1.

Appendix

Derivation of eq 10 from eq 7 is as follows:

$$\frac{\mathrm{d}(\ln k_{ij})}{\mathrm{d}(\ln K_{ij})} = \frac{\mathrm{d}a}{\mathrm{d}(\ln K_{ij})} + 0.5 + 2c(\ln K_{ij})^2 + (\ln K_{ij})^2 = \frac{\mathrm{d}c}{\mathrm{d}(\ln K_{ij})} \tag{A-1}$$

$$\frac{\mathrm{d}a}{\mathrm{d}(\ln K_{ij})} = -\frac{\mathrm{d}\lambda}{\mathrm{d}(\ln K_{ij})} \Big/ (4RT) \tag{A-2}$$

$$\lambda = (\lambda_{ii}/2) + (\lambda_{jj}/2) \tag{A-3}$$

Since A$_j^+$ is invariant $\mathrm{d}\lambda_{jj}/\mathrm{d}(\ln K_{ij})$ is 0.

$$\lambda_{ii} = 4(\Delta G_{ii}^* - W^r)$$

$$\lambda_{ii} = -4RT\left(\ln k_{ii} + \ln\left(\frac{h}{kT}\right)\right) - 4W^r \tag{A-4}$$

$$\frac{\mathrm{d}\lambda}{\mathrm{d}(\ln K_{ij})} = -2RT\,\frac{\mathrm{d}(\ln k_{ii})}{\mathrm{d}(\ln K_{ij})} \tag{A-5}$$

$$\frac{\mathrm{d}a}{\mathrm{d}(\ln K_{ij})} = 0.5\frac{\mathrm{d}(\ln k_{ii})}{\mathrm{d}(\ln K_{ij})} \tag{A-6}$$

$$\frac{\mathrm{d}c}{\mathrm{d}(\ln K_{ij})} = \frac{RT}{4\lambda^2}\,\frac{\mathrm{d}\lambda}{\mathrm{d}(\ln K_{ij})} \tag{A-7}$$

$$\frac{\mathrm{d}c}{\mathrm{d}(\ln K_{ij})} = -0.5\left(\frac{RT}{\lambda}\right)^2 \frac{\mathrm{d}(\ln k_{ii})}{\mathrm{d}(\ln K_{ij})} \tag{A-8}$$

When the definitions of a, $(\tau - 1)$, and c, along with the values of the derivatives obtained in eq A-6 and eq A-8, are substituted in eq A-1, eq 10 is obtained.

Registry No. 1a, 89321-40-4; **1b**, 85289-84-5; **1c**, 87513-46-0; **1d**, 89321-41-5; **1e**, 89321-42-6; **1f**, 89321-43-7; **1g**, 89321-44-8; **1h**, 89321-45-9; **1i**, 46176-64-1; **3a**, 84811-85-8; **3b**, 47072-02-6; 10-methylacridan, 4217-54-3.

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