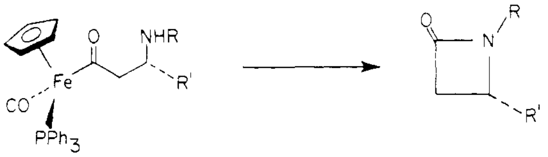
for stereoselectivity by 270-MHz ^1H NMR. Most of the condensations were conducted at −42 °C (dry ice–CH_3CN); however, lower temperature significantly improved the diastereoselection in the one case investigated (compare entries 1 and 2, Table I). The mass balance of each reaction is included in the table to underscore the fact that the observed diastereoselectivities were not perturbed by significant decomposition of the products. Extensive optimization of product yields has not been investigated.

Rigorous structure proof establishing the major diastereomer formed by condensation of enolate **3** (M = Li) with (*E*)-PhCH═NPh as **4a** (R = R′ = Ph) was secured by X-ray diffraction.[13] Assignment of structure **4a** to the major diastereomer of the other imine condensation products rests upon comparison of their 270-MHz ^1H NMR spectra with those obtained for **4a** and **4b** (R = R′ = Ph). All major diastereomers **4a** showed the higher field methylene hydrogen absorption (H_a, H_b) coupled to the methine H_c with a smaller vicinal coupling constant than the corresponding coupling of H_c to the lower field methylene hydrogen. The minor diastereomer absorptions that could be clearly observed in entires 1, 3, and 8 in Table I had reversed magnitudes of vicinal coupling of the methine H_c to the higher field and lower field methylene hydrogens. These collective data are consistent with all major diastereomers possessing the same relative stereochemistry as that confirmed for **4a** (R = R′ = Ph).

Selective formation of diastereomer **4a** can be qualitatively rationalized by formation of the condensation products as shown in Scheme I. Coordination of the nitrogen of the (*E*)-imine to the aluminum enolate would provide a cyclic transition state for product formation in which the substituent on the carbon of the imine double bond is forced toward the chiral iron. The presumption that bond formation occurs from a conformation of the enolate that places the very bulky PPh_3 180° away from the approaching imine leads to discrimination between the two diastereotopic faces of the enolate (Scheme I, **5a** and **5b**). Therefore, selective reaction should occur from **5a** that would lead to selective formation of diastereomer **4a**.

The β-aminoiron acyls prepared herein should provide β-lactams on oxidative decomposition since Rosenblum has shown that oxidation of β-aminoiron alkyls (prepared by addition of amines to cationic (η-C_5H_5)$Fe(CO)_2$ alkene complexes) gives β-lactams presumably via oxidatively assisted migratory insertion to transient iron(III) β-aminoacyls.[14] In a brief unoptimized study we have treated **4a** (R = R′ = Ph and R = *n*-Pr, R′ = Ph) with I_2/R_3N in CH_2Cl between −42 and 0 °C and observed facile β-lactam formation (eq 2).



(2)

R = R' = Ph; 80 %
R = nPr, R' = Ph; 70 %

The present diastereoselective condensations using racemic iron acyl **2** should extend to enantioselective condensations using optically active **2** and thus might prove significant in asymmetric organic synthesis. Complete details of this study will be published as a full paper.

Acknowledgment. This project was supported, in part, by the National Science Foundation under Grant CHE-8305055.

Supplementary Material Available: Spectral and analytical data for iron complexes and β-lactams and a typical experimental procedure for β-lactam formation (5 pages). Ordering information is given on any current masthead page.

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(13) Complete details of the X-ray analysis will accompany the full paper.

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Application of Marcus Theory to Metal Ion Catalyzed Group Transfer Reactions

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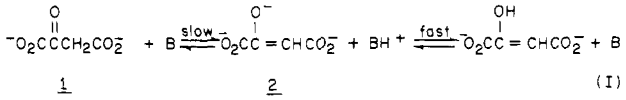
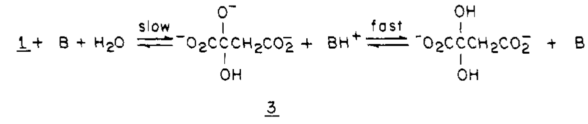
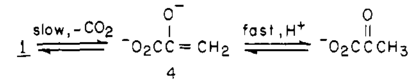
Particularly pertinent to questions regarding the role that metal ions play in biological systems are those model reactions in which complexing metal ions act on a substrate in concert with another catalyst (often a general base) to yield enhanced catalysis.[1-5] We have observed such behavior for the rates of enolization (eq I) and hydration (eq II) of oxalacetate ($oxac^{2-}$) and found that these rates, along with those for decarboxylation (eq III),[6,7] conform to the Marcus equation for group transfer.[8] This equation relates the free energy of activation to $\Delta G°$, the thermodynamic change in free energy, and $\Delta G_0^{\ddagger}$, the average of the self-exchange (or intrinsic) barriers for substrate and catalyst. Available information regarding complex stabilities[9] permits accurate predictions of metal ion induced changes in $\Delta G°$. No quantitative guidelines exist for the effect on $\Delta G_0^{\ddagger}$, because the Marcus relation appears not to have been previously applied to these types of reactions. We report here that the influence of Mg^{II} (and also of Zn^{II} in decarboxylation) on reaction rates is essentially accounted for by the *thermodynamics* of the interactions with the strong chelating centers formed on the intermediates, **2**, **3**, **4**, and the $\Delta G_0^{\ddagger}$ values for a given catalytic mode are metal ion independent. This discovery should apply to other systems, and once $\Delta G_0^{\ddagger}$ for a reaction pathway is determined, say, from a single rate measurement on uncomplexed substrate, it appears possible to make reasonable predictions of rate constants for similar paths involving complexed substrate and general acids or general bases.



$$\underset{\underline{1}}{{}^{-}O_2C\overset{\overset{O}{\|}}{C}CH_2CO_2^-} + B \overset{\text{slow}}{\rightleftharpoons} \underset{\underline{2}}{{}^{-}O_2C\overset{\overset{O^-}{|}}{C}=CHCO_2^-} + BH^+ \overset{\text{fast}}{\rightleftharpoons} {}^{-}O_2C\overset{\overset{OH}{|}}{C}=CHCO_2^- + B \qquad (I)$$



$$\underline{1} + B + H_2O \overset{\text{slow}}{\rightleftharpoons} \underset{\underline{3}}{{}^{-}O_2C\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}CH_2CO_2^-} + BH^+ \overset{\text{fast}}{\rightleftharpoons} {}^{-}O_2C\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CO_2^- + B \qquad (II)$$



$$\underline{1} \overset{\text{slow, }-CO_2}{\rightleftharpoons} \underset{\underline{4}}{{}^{-}O_2C\overset{\overset{O^-}{|}}{C}=CH_2} \overset{\text{fast, }H^+}{\rightleftharpoons} {}^{-}O_2C\overset{\overset{O}{\|}}{C}CH_3 \qquad (III)$$

Forward rate constants for base-catalyzed enolization[10-13] are given in Table I. For free $oxac^{2-}$, base catalysts having oxygen donor atoms, imidazole, and the hindered tertiary amine, 2-(diisopropylamino)ethanol (DPEA), show normal behavior conforming to a Brønsted relationship.[10,12] Less hindered tertiary amines show higher catalytic rates relative to their basicities[10-12] and are claimed[12] to react via a carbinol amine mechanism. In Table I the rate constants for unprotonated and monoprotonated *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEN and $HTMEN^+$)

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Table I. Forward Catalytic Rate Constants and Self-Exchange Barriers for Enolization

		oxac^{2-}			Mg(oxac)		
catalyst	pK_a^{HB}	k_f^a	ref	$\Delta G_0^{\ddagger\,b}$	k_f^a	ref	$\Delta G_0^{\ddagger\,b}$
OH^-	15.75	80	*d*	15	1.3×10^5	*d*	14
PO_4^{3-}	11.35	1.0	12	13			
DPEA	10.25	0.4	12	15			
CO_3^{2-}	9.77	0.088	12	14			
imidazole	7.2	0.062	10	14			
HPO_4^{2-}	6.7	0.014	12	13			
AcO^-	4.75	~0.005	10^c	~13	1.1	13	14
TMEN	9.35	80	d	11	1.5×10^3	*d*	13
HTMEN$^+$	6.15	9.7	d	11	1.2×10^2	*d*	12

^{a} $M^{-1}\ s^{-1}$. ^{b} kcal mol^{-1}. ^{c} Approximate value. ^{d} This work.

are those associated with the addition of amine to the oxac^{2-} keto group.[12] Evaluations of $\Delta G°$ for catalysis by a given base were made using the pK_a^{HB} given in the table and pK_a values determined to be 13.3 for oxac^{2-} and 8.0 for Mg(oxac).[14]

Those base catalysts that obey the Brønsted relationship yield values of $\Delta G_0^{\ddagger}$[15] lying in the range 14 ± 1 kcal mol^{-1}, while TMEN and HTMEN$^+$ show a distinctly lower apparent barrier height of 11 kcal mol^{-1}. In contrast, complexing to Mg^{II} brings about substantial increases in the rates for OH^- and AcO^- catalysis, but the $\Delta G_0^{\ddagger}$ values are found to remain at 14 kcal mol^{-1}. The influence of Mg^{II} on the pK_a of oxac^{2-} quantitatively accounts for the rate increases. Furthermore, the value of 13 kcal mol^{-1} for the TMEN reaction with Mg(oxac) suggests that the increase in oxac^{2-} acidity may cause tertiary amines to revert to the mode shown in (I).

Hydration rates are dominated by OH^- and H_2O catalysts,[11,12] but we have found weak catalysis by TMEN and HTMEN$^+$. $\Delta G_0^{\ddagger}$ values were calculated by using estimated hydrolysis constants pertaining to (II) of $10^{-19.7}$ M for oxac^{2-} and $10^{-15.2}$ M for Mg(oxac). The results are listed in order of catalyst, observed rate constant, and $\Delta G_0^{\ddagger}$ (kcal/mol). oxac^{2-}: OH^-, 480 $M^{-1}\ s^{-1}$, 10; H_2O, 0.03 s^{-1}, complex no.; TMEN, 0.26 $M^{-1}\ s^{-1}$, 9; HTMEN$^+$, 0.16 $M^{-1}\ s^{-1}$, 7. Mg(oxac): OH^-, 1.0×10^6 $M^{-1}\ s^{-1}$, 9; H_2O, 0.6 s^{-1}, complex no.; HTMEN$^+$, 3.2 $M^{-1}\ s^{-1}$, 9. Thus, two of the rate constants for oxac^{2-} and two for Mg(oxac), although spanning 7 orders of magnitude, give 9–10 kcal mol^{-1} for $\Delta G_0^{\ddagger}$. Discrepant results for the action of HTMEN$^+$ and H_2O on oxac^{2-} are brought into mutual accord when pathways involving the conjugate bases and H(oxac)$^{-1}$ are assumed. These last pathways are expected to be slower with complexed oxac^{2-} owing to a decrease in basicity, and relatively small rate increases are seen to be effected by Mg^{2+} on H_2O and HTMEN$^+$ catalysis. Indeed, the latter catalyst appears to serve as a base catalyst toward Mg(oxac).

Intrinsic barrier heights for decarboxylation were obtained from an expression that relates the barrier to the forward and backward rate constants.[18] Forward rate constants for CO_2 loss are 1.66 $\times 10^{-5}$ (oxac$^{2-}{}_{keto}$),[19] 0.0023 (Mg(oxac)$_{keto}$), and 0.045 s^{-1} (Zn(oxac)$_{keto}$). With the aid of recently acquired data,[20] 6.8×10^{-7} M has been assigned the equilibrium constant for oxac^{2-} $\rightleftarrows$ **4** + $CO_{2(aq)}$.[21] This value together with estimates of $10^{5.0}$ and $10^{7.0}$ M^{-1} for the binding constants of Mg^{2+} and Zn^{2+} to **4** enable the backward rate constants to be evaluated. The respective results for $\Delta G_0^{\ddagger}$ are 19, 19, and 18 kcal mol^{-1}. Thus decarboxylation represents a third example in which substantial metal ion induced changes in a reaction rate may be attributed solely to the effect on the thermodynamics of the reaction.

Acknowledgment. We thank the National Science Foundation for partial support of this work.

Registry No. oxac^{-2}, 149-63-3; Mg(oxac), 65636-56-8; Zn(oxac), 88295-82-3.

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[15] To apply the Marcus equation the rate-limiting reactions described by (I) and (II) were broken down into the following steps:

$$\text{oxac}^{2-} + \text{B} \underset{}{\overset{K_{1c}}{\rightleftarrows}} \text{oxac}^{2-}\cdots\text{B} \xrightarrow[\text{slow}]{k} (\text{oxac})\text{H}^{3-}{}_{-1}\cdots\text{HB}^+ \overset{1/K_{2c}}{\rightleftarrows} (\text{oxac})\text{H}^{3-}{}_{-1} + \text{HB}^+$$

Corrections to $\Delta G°$ for the free energies of forming the precursor and successor cage complexes were applied after K_{1c} and K_{2c} were evaluated using the Fuoss equation.[16] The preexponential coefficient was taken to be 0.1 to be consistent with Albery's[17] treatment of neutral species. A distance of 6 Å in the exponential term seemed to satisfactorily correct for electrostatic effects on the rates. The observed activation barrier was evaluated from the reduced constant, k/K_{1c}. The self-exchange barrier for buffer is ca. 5 kcal mol^{-1}.

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[21] $K_{III} = [\mathbf{4}][CO_2]/[\mathbf{1}] = k_fK_1K_2/k_bK_a$, where $K_1 = [\text{pyr}^-][HCO_3^-]/[\mathbf{1}] = 3.5 \times 10^4$;[22] $K_2 = [H^+][\mathbf{4}]/[H\mathbf{4}] = 1.0 \times 10^{-12}$, using the Taft parameters[23] to estimate the displacement from 11.1, the pK_a assigned to vinyl alcohol;[24,25] $K_a = [H^+][HCO_3^-]/[CO_2]_{aq} = 4 \times 10^{-7}$,[9a] pyr$^-$ (AcO^-) → H**4**, $k_f = 5 \times 10^{-6}$ $M^{-1}\ s^{-1}$;[2] H**4** (AcO^-) → pyr$^-$, $k_b = 0.64$ $M^{-1}\ s^{-1}$.[20]

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Aluminum Alkyls and Transition-Metal Hydrides: "Nonclassical" Adduct Structure and Catalysis of Hydrogen Migration

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An early, and now classic, demonstration of transition-metal basicity derives from the observation[1-4] that the d^2 complexes Cp_2MH_2 (M = Mo, W) react with Al_2Me_6 to form an adduct, often drawn explicitly with a dative bond (I).[5] The d^0 hydride

$$\underset{\text{I}}{Cp_2H_2W{\rightarrow}AlMe_3} \qquad \underset{\text{II}}{Cp_3Zr\text{-}H\text{-}AlMe_3}$$

Cp_3ZrH has been shown to have structure II.[6] We now report

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