

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

catalyst	pK _a ^{HB}	oxac ²⁻			Mg(oxac)		
		k _f ^a	ref	ΔG _o ^{‡b}	k _f ^a	ref	ΔG _o ^{‡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 oxac²⁻ keto group.¹² Evaluations of ΔG^o 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 oxac²⁻ and 8.0 for Mg(oxac).¹⁴

Those base catalysts that obey the Brønsted relationship yield values of ΔG_o^{‡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 ΔG_o[‡] values are found to remain at 14 kcal mol⁻¹. The influence of Mg^{II} on the pK_a of oxac²⁻ 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 oxac²⁻ acidity may cause tertiary amines to revert to the mode shown in (I).

Hydration rates are dominated by OH⁻ and H₂O catalysts,^{11,12} but we have found weak catalysis by TMEN and HTMEN⁺. ΔG_o[‡] values were calculated by using estimated hydrolysis constants pertaining to (II) of 10^{-19.7} M for oxac²⁻ and 10^{-15.2} M for Mg(oxac). The results are listed in order of catalyst, observed rate constant, and ΔG_o[‡] (kcal/mol). oxac²⁻: OH⁻, 480 M⁻¹ s⁻¹, 10; H₂O, 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 × 10⁶ M⁻¹ s⁻¹, 9; H₂O, 0.6 s⁻¹, complex no.; HTMEN⁺, 3.2 M⁻¹ s⁻¹, 9. Thus, two of the rate constants for oxac²⁻ and two for Mg(oxac), although spanning 7 orders of magnitude, give 9-10 kcal mol⁻¹ for ΔG_o[‡]. Discrepant results for the action of HTMEN⁺ and H₂O on oxac²⁻ 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 oxac²⁻ owing to a decrease in basicity, and relatively small rate increases are seen to be effected by Mg²⁺ on H₂O 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 CO₂ loss are 1.66 × 10⁻⁵ (oxac²⁻_{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 oxac²⁻ ⇌ 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 Mg²⁺ and Zn²⁺ to 4 enable the backward rate constants to be evaluated. The respective results for ΔG_o[‡] 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. oxac²⁻, 149-63-3; Mg(oxac), 65636-56-8; Zn(oxac), 88295-82-3.

(20) Miller, B. A., unpublished results obtained in these laboratories.

(21) K₁₁₁ = [4][CO₂]/[I] = k_fK₁K₂/k_bK_a, where K₁ = [pyr][HCO₃⁻]/[I] = 3.5 × 10³;²² K₂ = [H⁺][4]/[H4] = 1.0 × 10⁻¹², using the Taft parameters²³ to estimate the displacement from 11.1, the pK_a assigned to vinyl alcohol;^{24,25} K_a = [H⁺][HCO₃⁻]/[CO_{2(aq)}] = 4 × 10⁻⁷,²⁶ pyr (AcO⁻) → H4, k_f = 5 × 10⁻⁶ M⁻¹ s⁻¹,² H4 (AcO⁻) → pyr⁻, k_b = 0.64 M⁻¹ s⁻¹.²⁰

(22) Wood, H. G.; Davis, J. J.; Lochmuller, H. J. *Biol. Chem.* **1966**, *241*, 5692.

(23) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. "pK_a Prediction for Organic Acids and Bases"; Chapman and Hall: New York, 1981.

(24) Capon, B.; Zucco, C. *J. Am. Chem. Soc.* **1982**, *104*, 7567.

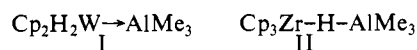
(25) Guthrie, J. P.; Gillmore, P. A. *Can. J. Chem.* **1979**, *57*, 240.

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

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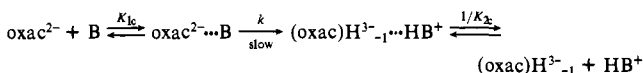
An early, and now classic, demonstration of transition-metal basicity derives from the observation¹⁻⁴ that the d² complexes Cp₂MH₂ (M = Mo, W) react with Al₃Me₆ to form an adduct, often drawn explicitly with a dative bond (I).⁵ The d⁰ hydride



Cp₃ZrH has been shown to have structure II.⁶ We now report

(14) Tate, S. S.; Grzybowski, A. K.; Datta, S. P. *J. Chem. Soc.* **1964**, 1372, 1381.

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



Corrections to ΔG^o 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's¹⁷ 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.

(16) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

(17) Albery, W. J. *J. Chem. Soc. Faraday Trans. 1* **1982**, *78*, 1579. For a general review, see: Albery, W. J. *Ann. Rev. Phys. Chem.* **1980**, *31*, 227.

(18) Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2660.

(19) Gelles, E. J. *Chem. Soc.* **1956**, 4736.

(1) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

(2) Johnson, M. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1966**, *88*, 301 and references therein.

(3) Brunner, H.; Wailes, P. C.; Kaesz, H. D. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 125.

(4) Storr, A.; Thomas, B. S. *Can. J. Chem.* **1971**, *49*, 2504.

(5) Note that the structure drawn previously bears no relation to the shape of the HOMO of d² Cp₂MH₂ species, shown later to lie outside the HMH angle. For leading references, see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.