other chromoacerands[12] and ionophores.[25]

Supplementary Material Available: Full listings of fractional atomic coordinates and interatomic bond distances of the **2a**-piperazine 1:1 saltex (4 pages). Ordering information is given on any current masthead page.

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The Aminolysis of Methyl Formate with Aniline: Evidence for Catalysis by a Trapping Mechanism[1]

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It has been proposed that general base catalysis of ester aminolysis can involve rate-limiting diffusion-controlled proton removal from the addition intermediate $T^{\pm}$.[2,3] However, this has not been directly demonstrated for bimolecular ester aminolysis, although related reactions such as the hydrazinolysis of acetylimidazole[4] and the hydroxylaminolysis of iminium cations[5] are catalyzed by diffusion-controlled proton removal by bases. The general base-catalyzed cyclization of methyl *o*-aminophenyl propionate shows rate constants independent of base strength for three bases of pK 6-10, consistent with catalysis by diffusion-controlled proton transfer for an intramolecular ester aminolysis.[6] Buffer catalysis, with enhanced activity of bifunctional catalysts, has been observed for breakdown to amine and ester of the intermediate formed from the hydration of ethyl *N*-phenylformimidate,[7] and there is evidence that diffusion-controlled proton transfer can be product determining in the partitioning of other imidates.[2,8] We describe here direct evidence that the aminolysis of methyl formate by aniline involves enforced catalysis by strong bases that is encounter-limited. Catalysis by weaker bases involves partially rate-limiting proton transfer with $T^{\pm}$, and still weaker bases react with rate-limiting diffusional separation of the encounter complex $T^{-}\cdot BH^{+}$.[2,9] The proton-transfer step is responsible for a solvent deuterium isotope effect on general base catalysis with a maximum at pK_{BH} ~ 5.

The aminolysis of methyl formate by aniline shows strong catalysis by buffers at concentrations of <50 mM. Figure 1A shows the Brønsted plot for general base catalysis of aminolysis by oxygen bases of pK_{BH} from 1 to 9. Rate constants for monofunctional catalysts (solid symbols) follow a curve that approaches slopes of $\beta = 0$ and $\beta = 1.0$ for strong and weak bases, respectively. Rate constants for bifunctional catalysts (open symbols) follow a line of slope $\beta = 0$. While rate constants for bifunctional bases are similar to those for strong monofunctional catalysts, bifunctional catalysts of p$K < 4.5$ are more active than their monofunctional counterparts by up to 10^3-fold.

Figure 1B shows the solvent deuterium isotope effects for general base catalysis. Monofunctional catalysts (solid circles) display an isotope effect maximum of $k_B^{HOH}/k_B^{DOD} = 5$ at pK_{BH} = 5.3, with little or no isotope effect for catalysis by strong or very weak base catalysts. Four bifunctional catalysts show isotope effects in the range of 1.9-2.5.

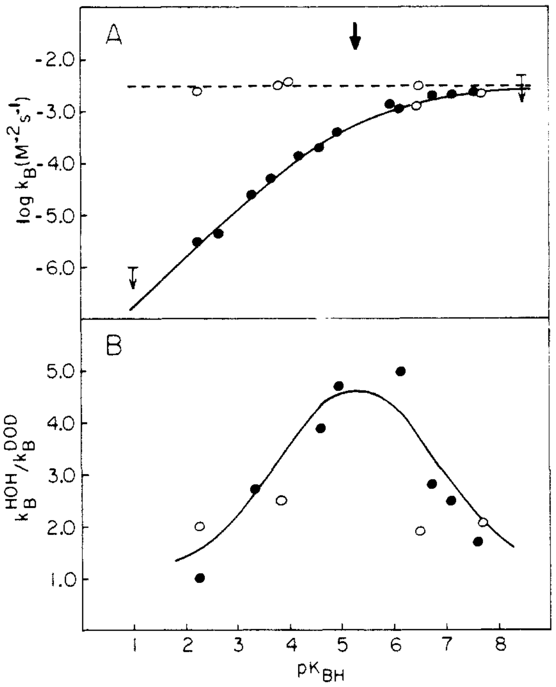
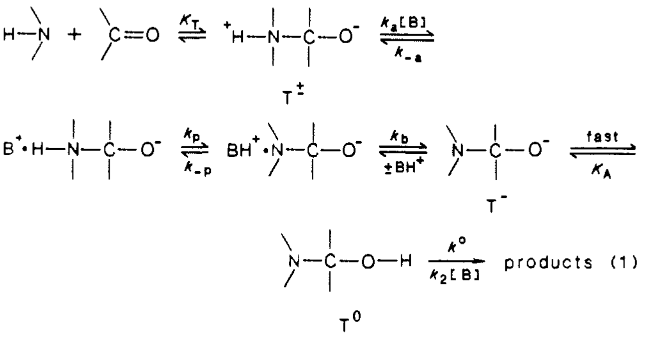


Figure 1. (A) Brønsted plot for general base catalysis of the aminolysis of methyl formate by aniline at 25 °C, ionic strength 1.0 (KCl; methylarsonate in NaCl), 0.1 M MOPS buffer. Experiments were performed between pH 7 and 8, where $T^{\pm}$ conversion to T^0 is rate-limiting.[2,17] Initial rates of formanilide formation were determined at 240 nm with aliquots of the reaction mixture quenched in 0.1 M HCl.[18] Closed symbols: monofunctional catalysts (carboxylates, cacodylate, and phosphonate dianions); open symbols: bifunctional catalysts (fluoroacetone hydrates, phosphonate, bicarbonate, methylarsonate monoanions, and phosphate dianion). The solid line was calculated for a trapping mechanism.[14] The arrow at pK = 5.3 shows the pK of $T^{\pm}$ which best fits the data.[13] (B) Solvent deuterium isotope effects for general base catalysis of the aminolysis of methyl formate by aniline. Solid symbols: monofunctional catalysts; open symbols: bifunctional catalysts. The solid line represents the isotope effect assuming a constant value of k_H/k_D = 6.5 for the proton-transfer step, k_p.[14]

The nonlinear Brønsted plot for monofunctional bases fits an "Eigen curve" for rate-limiting diffusion-controlled proton transfers.[10] This is consistent with the trapping mechanism shown in eq 1 in which the different regions of the Brønsted plot are represented by three different rate-limiting steps: k_a, k_p, and k_b for strong, weak, and very weak bases, respectively. The isotope effect maximum appears in the region in which k_p is partially rate-limiting, which is typical for proton transfer between electronegative atoms.[5,11,12] The break in the Brønsted plot from slope $\beta = 1.0$ to $\beta = 0$ for monofunctional catalysts occurs at pK_{BH} = 5.3 (arrow, Figure 1A), which is consistent with the calculated[13]



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pK = 5.4 for T$^{\pm}$. The solid line in Figure 1A shows the Brønsted correlation calculated[14] for the trapping mechanism of eq 1 and pK = 5.3 for T$^{\pm}$; it gives a satisfactory fit to the experimental data.

The Brønsted slope of $\beta = 0$ for bifunctional catalysts is consistent with diffusion-controlled encounter being largely or entirely rate-limiting, regardless of buffer pK. A rapid bifunctional proton transfer that converts T$^{\pm}$ to T^0 can explain why proton transfer and diffusional separation do not become rate-limiting for very weak bases.[15,16]

The results presented here provide what we believe to be the first direct evidence that the bimolecular aminolysis of an ester involves a trapping mechanism, in which general base catalysis involves rate-limiting diffusion-controlled proton transfer.

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(13) A pK of T$^{\pm}$ = 5.4 ± 1.0 was calculated by using procedures described in the following: Fox, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1436.

(14) The theoretical curve that provides a satisfactory fit for the data in Figure 1A was calculated with eq 2 from ref 14, with $pK_{T\pm} = 5.3$, $K_1 = 3 \times 10^{-12}$ M^{-1}, $k_a = 10^9$ M^{-1} s^{-1}, $k_{-a} = k_b = 10^{10}$ s^{-1}, $\log k_p = 9.4 + 0.5\Delta pK$, and $\log k_{-p} = 9.4 - 0.5\Delta pK$ ($\Delta pK = pK_A - pK_{T\pm}$). The solid curve in Figure 1B was calculated assuming $k_H/k_D = 6.5$ for k_p and k_{-p}.

(15) Barnett, R. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 2358.

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(17) The aminolysis of alkyl esters shows a change in rate-limiting step on a pH-log rate profile (ref 2, Blackburn, G. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 2638). This has been attributed to rate-limiting breakdown of the neutral intermediate T^0 to products at low pH, changing to rate-limiting formation of T^0 from T$^{\pm}$ at high pH.[2] Between pH 7 and 9, the uncatalyzed aminolysis of methyl formate by aniline is pH-independent (results not shown) and is consistent with the latter step being rate-limiting as previously described.[2]

(18) Plots of observed second-order rate constants against total buffer concentration show curvature with increasing buffer concentration, consistent with a change in rate-limiting step to T^0 breakdown at high buffer concentrations. Third-order rate constants for base catalysis at low buffer concentrations, k_B, were determined by fitting the data to eq 2. The rate constants

$$k_2\text{obsd} = K_T \frac{(k_s + k_1[B])(k^0 + k_2[B])}{(k_{-s} + k_{-1}[B]) + (k^0 + k_1[B])} \qquad (2)$$

k_s, k_{-s}, and k_1, k_{-1} are buffer independent and base-catalyzed rate constants, respectively, for interconversion of T$^{\pm}$ to T^0, whereas k^0 and k_2 are the buffer independent and base-catalyzed rate constants, respectively, for the breakdown of T^0 to products as outlined in eq 1, and $k_B = K_T k_1$. Rate constants for general base catalysis were obtained by either the determination of rate constants for buffer catalysis at several fractions of buffer base and extrapolating to 100% base or by a single experiment at a pH value >1.5 units above the buffer pK.

Strained Rings as a Source of Unsaturation: Polybenzvalene, a New Soluble Polyacetylene Precursor

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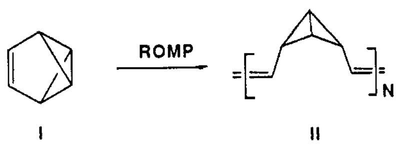
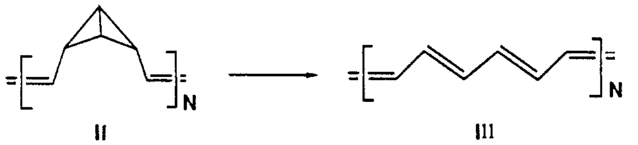
Conductive polymers currently represent an active area of research in polymer science.[1] Polyacetylene (PA) has been at center stage throughout the evolution of this field,[2] with a conductivity that can be increased with doping to values that rival copper.[3] PA and many other conductive polymers are insoluble, infusable materials with low tensile strength, and thus the manipulation of these materials into useful shapes and morphologies is limited. One solution to these material and processing problems has been the use of soluble precursor polymers that can be transformed into conductive polymers.[4] Precursor routes have afforded the synthesis of materials with higher molecular weights and highly ordered anisotropic morphologies.[4] One major drawback to the existing precursor routes is that they generally rely on the extrusion of molecular fragments. These extruded fragments may comprise a substantial fraction of the total mass and thus potentially limit the usefulness of these processes. The development of precursor routes that do not rely on the extrusion of small molecules is therefore desirable. We report herein the synthesis of polybenzvalene, an unusual polymer that can be transformed into PA without the extrusion of molecular fragments.

Scheme I



Scheme II



Polybenzvalene (II) was synthesized by the ring opening metathesis polymerization (ROMP) of the highly reactive but readily available monomer benzvalene (I),[5] as shown in Scheme I. We have previously demonstrated the utility of ROMP with titanocene metallacycle catalysts in the synthesis of living polymers,[6a] block copolymers,[6b] and a cross-conjugated conducting polymer precursor.[6c] However, these titanium catalysts proved ineffective in the polymerization of I.[7] The ROMP of I has only been made possible by the development of non-Lewis acidic[8] well-defined active tungsten alkylidene metathesis catalysts.[9,10] The catalytic systems of both Schrock[9] and Osborn[10] were effective for the ROMP of I. We have used the catalysts of Schrock[12] in our studies as a result of their selectivity for the formation of cis olefins.[9b]

II is an interesting material in its own right. The bicyclobutane moiety has approximately 64 kcal/mol of strain energy,[13] and thus the polymer has about 11 kcal of strain energy per carbon atom. High-energy polymers such as II may have applications in pro-

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(7) Reaction of I with titanocene alkylidenes resulted in metallacycles that were thermally unreactive at temperatures less than 80 °C. At these temperatures I is rapidly converted to benzene.

(8) I was found to react exothermically with Lewis acidic catalysts $WCl_6{:}Sn(Me)_4$, $WOCl_4{:}Sn(Me)_4$, and $((Me)_3CCH_2O)_2W(Br)_2CHC(Me)_3{:}GaBr_3$ to give a dark brown intractable material.

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(11) The non-Lewis acidic metathesis catalysts, $(CO)_5WC(OMe)Ph$ and $(CO)_5WC(Ph)_2$, in which the chain carrying species are not known or observed were investigated and found to be ineffective. However, these catalysts have been shown to be effective for other monomers: Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *J. Am. Chem. Soc.* **1980**, *102*, 7940 and 7942.

(12) The catalysts employed were $(RO)_2W(N(2,6\text{-}(i\text{-}Pr)_2Ph))CHC(Me)_3$ where R = *tert*-butyl, or hexafluoro-*tert*-butyl (ref 8). The catalysts were used at room temperature and −20 °C, respectively, in benzene or toluene and were found to give the same material by NMR (ref 15).

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