phosphorus ligands but without a plane of symmetry passing through the Pt–P bond(s) satisfies these observations. Furthermore, rapid equilibration of **6** and **7** via a turnstile or pseudorotation process cannot be occurring at 20 °C.

Octafluorocyclooctatetraene has been shown to be a novel ligand which undergoes oxidative addition reactions with low-valent transition metals. Its coordination chemistry should be as rich as that of its hydrocarbon analogue and is under continuing investigation.

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Supplementary Material Available: Tables of atomic positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Mechanism of Proton Transfer from Intramolecularly Hydrogen-Bonded Acids. Differences between Nitrogen-to-Oxygen and Nitrogen-to-Nitrogen Proton Transfer

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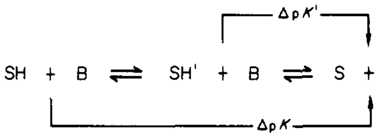
We wish to report that, using an isotropic tracer method to measure rates of proton transfer from the intramolecularly hydrogen-bonded conjugate acid of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene, we have obtained data which give a sharply curved biphasic Brønsted plot diagnostic of a two-step reaction mechanism; our results also indicate that nitrogen-to-nitrogen proton transfers are intrinsically slower than nitrogen-to-oxygen proton transfers.

It is well-known that incorporation of an acidic hydrogen into an intramolecular hydrogen bond slows its rate of reaction with external bases by several orders of magnitude. This diminished reactivity was originally explained by a two-step reaction mechanism in which the internal hydrogen bond is first broken to give an acid externally hydrogen bonded to solvent; this unstable intermediate then reacts with the proton acceptor in a normal fast reaction, but the rate of the overall process is slowed by the intermediate's low concentration.[1] It was later pointed out, however, that a single-step mechanism, in which the proton is transferred directly out of the intramolecular hydrogen bond, would also give a reduced rate because its transition state would have a tricoordinated hydrogen with an unfavorable nonlinear arrangement of forming and breaking bonds.[2]

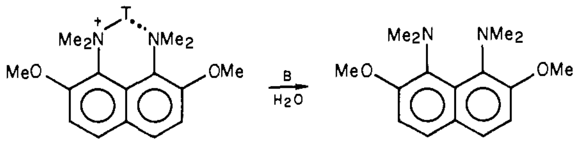
A choice between these two alternatives might be made on the basis of the characteristics expected for the second step of the stepwise mechanism: when the proton donor and the proton acceptor are both nitrogen or oxygen species, this step will give a biphasic Brønsted plot of the kind first observed by Eigen for normal acid–base reactions,[1] and it will also show a sharp isotope effect maximum.[3] In normal acid–base reactions these features appear where the pK_a difference between the proton donor and the protonated proton acceptor is zero, and in the present case this is the point at which $\Delta pK' = 0$, where $\Delta pK'$ refers to the pK_a difference for the actual proton-transfer step (eq 1). This point will be displaced in the uphill direction from the place where the overall pK_a difference between the intramolecularly hydrogen-bonded acid and the protonated proton acceptor, ΔpK in eq 1, is zero; the magnitude of this displacement is determined by the value of the preequilibrium constant and is in general appreciable.



$$\mathrm{SH} + \mathrm{B} \rightleftharpoons \mathrm{SH'} + \mathrm{B} \rightleftharpoons \mathrm{S} + \mathrm{HB} \qquad (1)$$

This complication makes observation of these features characteristic of the two-step mechanism difficult, inasmuch, as standard kinetic techniques, including fast reaction methods, are limited to the region a few pK units to either side of $\Delta pK = 0$. In the latter region the expected behavior of the two-step mechanism is less diagnostic: Brønsted plots will be monophasic and isotope effects will be constant and near unity. Measurements in this region have nevertheless been made; the results suggest reaction by a two-step mechanism in some cases,[4] but point to the simultaneous operation of both mechanisms in others.[5]

We wish to report that we have developed an isotopic tracer method of making measurements in the more diagnostic region near $\Delta pK' = 0$ and the results we have obtained indicate the operation of a two-step reaction mechanism. We prepared the conjugate acid of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene[6] (**1**) labeled with tritium in its acidic nitrogen–hydrogen bond and monitored the loss of this label to solvent in a wholly aqueous medium in the presence of basic catalysts (eq 2)



1

(2)

by quenching aliquots of reaction mixture, removing solvent by vacuum evaporation, and subjecting the residues to radioactive assay by liquid scintillation counting. This reaction is strongly uphill and therefore quite reversible at $\Delta pK' = 0$, but the overwhelmingly large pool of hydrogen in the solvent effectively prevents tritium from reentering the substrate.

Kinetic data obtained in this way follow the first-order rate law, as expected. The reaction shows general base catalysis, and standard treatment of the data gives the catalytic coefficients which are displayed in Figure 1 in the form of a Brønsted plot.[7] It may be seen that these rate constants disperse into two categories depending on whether the proton acceptor is an oxygen or a nitrogen base. The oxygen bases give a decidedly biphasic plot

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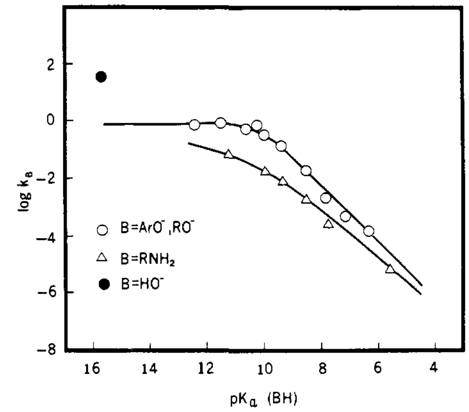

Figure 1. Brønsted plot for proton transfer from the conjugate acid of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene to external bases in aqueous solution at 25 °C. The oxygen bases (open circles) are, from left to right, $CF_3CH_2O^-$, CH_3CHNO^-, $C_6H_5CHNO^-$, 3,4-$(CH_3)_2C_6H_3O^-$, $C_6H_5O^-$, 4-$ClC_6H_4O^-$, 2-$ClC_6H_4O^-$, 2,4-$Cl_2C_6H_3O^-$, 4-$NO_2C_6H_4O^-$, 2,4,6-$Cl_3C_6H_2O^-$, and the nitrogen bases (triangles) are, from left to right, $(CH_2)_5NH$, $CH_3O(CH_2)_3NH_2$, $C_6H_5CH_2NH_2$, $(CH_3O)_2CHCH_2NH_2$, $CN(CH_2)_2NH_2$, and $CF_3CH_2NH_2$.

with a sharply curving portion joining limbs of zero and unit slope, as expected for a normal acid–base reaction.[1] Nitrogen bases react more slowly than oxygen bases of the same pK_a; part of this difference could be an electrostatic effect inasmuch as the oxygen bases are all negatively charged, but the more gradual curvature shown by the nitrogen bases indicates that these N-to-N proton transfers are also intrinsically slower than the N-to-O transfers of the other set. This is expected on the basis of the lower electronegativity and consequent poorer hydrogen-bond accepting ability of nitrogen bases.[1,8] The hydroxide ion shows an anomalously high reactivity, which again is the expected result for a normal acid externally hydrogen bonded to solvent reacting by a Grotthuss-chain mechanism.

These results are the expected behavior for the two-step reaction scheme of eq 1, and assignment of this mechanism confirms the conclusion reached in previous studies of the kinetics of protonation of 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene in Me_2SO–water solution.[4b] The pK_a of protonated 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene has also been estimated from measurements made in Me_2SO–water solution, but the result obtained, pK_a = 16.3,[6] is considerably less than the value, pK_a = 19–20, deduced for wholly aqueous solution from the position of the break in the present Brønsted plot (Figure 1) and the lowering of the horizontal limb of this plot from the value expected for an encounter-controlled reaction.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

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Metal Hydride Reductions via Single Electron Transfer. 2. Evidence for an Electron-Transfer Pathway in the Reactions of Simple and Complex Metal Hydrides of the Main Group Metals with Polynuclear Hydrocarbons

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Simple and complex metal hydrides of the main group metals are extensively used in synthetic organic chemistry as reducing agents.[1] Generally, their reactions with organic substrates such as ketones, unsaturated hydrocarbons, alkyl halides, etc., have been considered to proceed via a polar mechanism.[1,2]

Recently, reports from our laboratory[3] as well as others[4] have indicated the importance of single electron transfer (SET) in describing the mechanism of addition of main group organometallic compounds to ketones. More recently we have demonstrated that metal hydrides as well do indeed react with aromatic ketones via a single electron transfer mechanism.[5] In view of our recent findings with ketones, we decided to investigate single electron transfer of metal hydrides with organic substrates more broadly in order to test the scope of our initial findings. In this connection we are attempting to detect SET either by using a probe that will indicate a SET intermediate[6] or simply by selecting substrates whose radical intermediates formed by the electron transfer are stable enough to be studied spectroscopically. Here we wish to present evidence for the reactions of various simple and complex metal hydrides of the main group metals with polynuclear hydrocarbons via a SET mechanism as indicated by EPR and visible spectra of the intermediate radical anions.

In general, reactions of metal hydrides with organic substrates such as polynuclear hydrocarbons can be considered to involve two major steps. In the first step, the metal hydride reacts with the substrate via either SET to give a radical anion intermediate or by a polar mechanism transferring a hydride ion to the hydrocarbon. The next step of the SET or polar mechanism involves the conversion of the intermediate to the product. The present studies concentrate mainly on the first step of the reaction, and only preliminary results are presented here concerning the later stages of the reaction. To the best of our knowledge there is only one report available on the reaction of a metal hydryde ($LiAlH_4$) with a hydrocarbon (anthracene) to give a reduction product. The reported mechanism was thought to be polar.[7]

When a simple or complex metal hydride of a main group metal [$LiAlH_4$, $NaAlH_4$, AlH_3, MgH_2 and HMgCl] is allowed to react with a polynuclear hydrocarbon such as naphthalene, anthracene, phenanthrene, 2,3-benzanthracene, chrysene, benzo[*a*]pyrene, and perylene, in THF, a colored solution results. The rate of development of this color is dependent on the reactivity of the individual metal hydride, the reduction potential of the polynuclear hydrocarbon, the solvent, and the concentration of both reagents. Thus, the most reactive hydrides, $LiAlH_4$ and $NaAlH_4$, react with perylene (reduction potential = −1.64 eV) at 10^{-4} M concentration in THF at room temperature to give a blue intermediate, the intensity of which reaches ≃80% within 2 days [as determined by visible spectroscopy (λ_{max} 578 nm; Table I)] and increases slowly thereafter. On the other hand, naphthalene (reduction potential = −2.56 eV) produces only a trace amount of colored intermediate even at much higher concentration and after 10 days' reaction time. Similarly, the least reactive hydride reagent, HMgCl, reacts with perylene to give only about 20% intermediate after 15 days' reaction time. The colored intermediates obtained in these reactions are paramagnetic in nature and show well-resolved EPR spectra (Figure 1). The EPR and visible spectra were found to be similar to that of the radical anion, irrespective of the countercation.[8-10] For example, there is no appreciable difference in the spectrum of the reaction product of perylene with $LiAlH_4$ or $NaAlH_4$ (Table II). This observation is consistent

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