

to form *cis*-bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (**5**) as the rate-determining step. Pentaene **5** is known to undergo a disrotatory ring closure below  $-10\text{ }^{\circ}\text{C}$  to **1**, which dissociates to two molecules of benzene *in situ*.<sup>3a,11</sup>

Triplet benzene has been detected in the thermolysis of Dewar benzene by using 9,10-dibromoanthracene as the energy acceptor;<sup>12</sup> however, no triplet benzene was detected in the thermolysis of **2** under the same conditions. Although pathway 1 cannot be excluded at this moment, we favor the alternate pathway for the thermolysis of **2** under our experimental conditions. The detailed mechanisms of thermolysis of **1** and **2** are currently under investigation in our laboratory.

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### NMR Determination of Rates of Electron Pair Transfer through Bridges to or between Heteropoly Complex Centers. Enthalpy and Entropy Contributions to Activation. Evaluation of Equilibrium Constant for the Disproportionation Reaction

Mariusz Kozik and Louis C. W. Baker\*

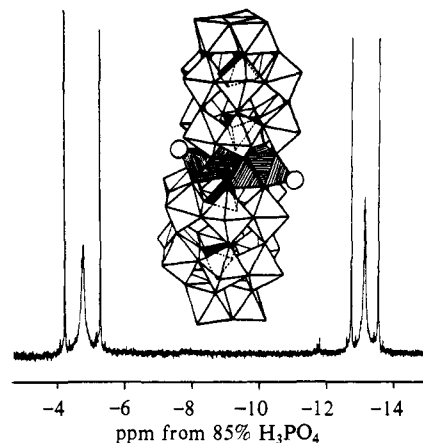
Department of Chemistry, Georgetown University  
Washington, DC 20057

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Substantial interest centers on electron transfer in polynuclear bridged complexes. Numerous heteropoly structures may be bridged by a variety of  $\text{MO}_n$  polyhedra and/or by organic bridging groups coordinated to transition metals that are integral parts of heteropoly structures.<sup>1-4</sup> Organic conducting groups are significant biochemically, and heretofore-little-investigated oxometalate bridges have importance for catalysis. Both have potential significance for investigation of electronic materials.

NMR studies of heteropoly blues<sup>5,6</sup> lead to an elegant method for elucidating activation energies and rates of electron transfer among heteropoly and other structures through a variety of bridges. The method is illustrated here with the  $[\text{P}_2\text{W}_{15}\text{O}_{49}-\text{Zn}_4\text{O}_{14}(\text{H}_2\text{O})_2-\text{O}_{49}\text{W}_{15}\text{P}_2]^{16-}$  complex,<sup>7</sup> Figure 1. The two  $\text{P}_2\text{W}_{15}\text{O}_{49}$  heteropolytungstate portions are bridged by a layer of four edge-sharing  $\text{Zn}^{2+}\text{O}_6$  octahedra. Analogous complexes are obtained<sup>7</sup> by replacing  $\text{Zn}^{2+}$  by  $\text{Co}^{2+}$  or  $\text{Cu}^{2+}$ . Ongoing investigations compare (1) abilities to transmit electrons and (2) relative equilibrium electron populations in the respective bridged heteropoly or other reducible moieties.

The  $^{31}\text{P}$  NMR spectrum of  $\text{Na}_{16}[\text{P}_2\text{W}_{15}\text{O}_{49}-\text{Zn}_4\text{O}_{14}(\text{H}_2\text{O})_2-\text{O}_{49}\text{W}_{15}\text{P}_2]$  solution consists of two sharp ( $\Delta\nu_{1/2} < 1.5\text{ Hz}$ ) lines, one from each pair of structurally identical P atoms.<sup>7</sup> The complex's first reduction wave represents a reversible four-electron



**Figure 1.** Inset: Structure<sup>7</sup> of  $[\text{P}_2\text{W}_{15}\text{O}_{49}-\text{M}_4^{2+}\text{O}_{14}(\text{H}_2\text{O})_2-\text{O}_{49}\text{W}_{15}\text{P}_2]^{16-}$ ,  $\text{M}^{2+} = \text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , or  $\text{Cu}^{2+}$ . Each vertex of an octahedron locates the center of an oxygen atom. Each white octahedron contains a W atom. Each hatched octahedron contains a  $\text{M}^{2+}$  atom. The four interior  $\text{PO}_4$  tetrahedra are shown in black and by dotted outlines. The locations of the two  $\text{H}_2\text{O}$  molecules coordinated to  $\text{M}^{2+}$  are circled. **Spectrum:**  $^{31}\text{P}$  NMR spectrum, taken on a Bruker AM-300WB spectrometer at 300 K, of mixture made by reduction, by two electrons per complex, of a 5 mM solution of  $\text{Na}_{16}[\text{P}_2\text{W}_{15}\text{O}_{49}-\text{Zn}_4\text{O}_{14}(\text{H}_2\text{O})_2-\text{O}_{49}\text{W}_{15}\text{P}_2]$  in 0.5 M lithium acetate buffer, pH 4.3, 20%  $\text{D}_2\text{O}$ . Outer pair of lines, oxidized complex; inner pair of lines, 4e-reduced complex; central lines in each group, 2e-reduced complex. The downfield set of three lines is for the P's nearer the  $\text{Zn}_4\text{O}_{14}(\text{H}_2\text{O})_2$  bridge.

process at a single cathodic potential ( $-0.50\text{ V}$  vs. SCE). The complex was reduced by just four electrons by constant potential electrolysis. This places two spin-coupled electrons in each heteropolytungstate end of the complex, forming a typical heteropoly blue.<sup>5,6</sup> The added electrons, delocalized on the NMR time scale, are rapidly hopping among the 12 "belt" W atoms in each polytungstate portion.<sup>5</sup> This diamagnetic 4e-reduced product also exhibits two narrow  $^{31}\text{P}$  NMR lines, the signal from the inner pair of P atoms having been shifted to lower frequency by  $\sim 128\text{ Hz}$  ( $-1.05\text{ ppm}$ ) and that from the outer pair to higher frequency by  $\sim 98\text{ Hz}$  ( $+0.81\text{ ppm}$ ).

A reduction that involves only half as many Coulombs per mole of complex as does the 4e reduction produces a solution that contains a mixture of complexes: unreduced, 4e-reduced, and 2e-reduced. This is shown by its  $^{31}\text{P}$  NMR spectrum (Figure 1), which consists of six base-line-resolved lines: two sharp lines coinciding exactly with those from the unreduced species, two sharp lines coinciding exactly with those from the 4e-reduced species, and two much broader lines (one for each structural type of P). Each of the latter lines centers exactly midway between the pair of sharp lines for its kind of P. Neither chemical shifts nor line widths for any of these signals change with concentration or with proportion of the complex reduced. The widths of the central broader lines decrease with increasing temperature while the widths of the sharp lines remain constant. All the systems are always perfectly diamagnetic, as shown by the Evans NMR method for susceptibility.<sup>8</sup> Thus the added electrons' spins are always paired by multiroute superexchange.<sup>5</sup>

The broad NMR lines are therefore assigned to complexes which have two added electrons on one side of the  $\text{Zn}_4\text{O}_{16}\text{H}_4$  bridge and none on the other. The electrons are exchanging, with spins paired, between the two heteropoly ends of the complex via concerted penetration through the  $\text{Zn}_4\text{O}_{16}\text{H}_4$  bridge. The single broad peak, for each structurally similar pair of P's, results from coalescence of the signals from the two nonidentical ends of the 2e-reduced complex, the electron exchange rate being in the NMR intermediate/fast exchange time scale region.<sup>9</sup> The P's envi-

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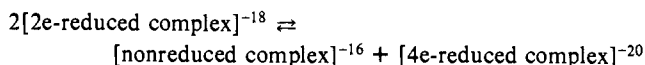
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ronments (and hence chemical shifts) in a reduced or nonreduced end of the complex are independent of whether the *other* end of the complex is reduced or not. The rate of the concerted exchange is calculable from the line widths.<sup>6,9</sup>

The disproportionation equilibrium constant for



was evaluated from peak areas for each species. In the present case both bridged heteropoly portions of the nonreduced complex are identical, and in the 2e-reduced species there is negligible electronic coupling energy between the two portions.<sup>10</sup> No new electronic transition (UV-vis, near-IR) was observed. Therefore the disproportionation equilibrium constant should be 0.25 as statistically dictated,<sup>10</sup> which is (within  $\pm 0.01$ ) the experimental value<sup>11</sup> at several different extents of total reduction and several temperatures.

**Kinetics.** Signals from the P's nearer the  $\text{Zn}_4\text{O}_{16}\text{H}_4$  bridge, being somewhat more widely spaced, were used for kinetic analysis. Their  $\Delta\nu_{1/2}$ 's for nonreduced and 4e-reduced species (1.1 and 1.4 Hz, respectively) were constant, proving intercomplex exchange rates negligible.  $\Delta\nu_{1/2}$ 's for the 2e-reduced species at five temperatures were the following: 300 K, 12.9 Hz; 310 K, 6.0 Hz; 320 K, 4.2 Hz; 330 K, 2.3 Hz; 340 K, 1.5 Hz. At a given temperature  $\Delta\nu_{1/2} = 1/(\pi T_2)$ , where  $T_2$  is spin-spin relaxation time, and<sup>9</sup>

$$1/T_{2(2e)} = x_{(\text{red})}/T_{2(\text{red})} + x_{(\text{ox})}/T_{2(\text{ox})} + x_{(\text{red})}^2 x_{(\text{ox})}^2 (2\pi\Delta\nu)^2 (\tau_{(\text{red})} + \tau_{(\text{ox})})$$

where  $\Delta\nu$  = difference in hertz between the two sharp peaks,  $x_{(\text{red})} = x_{(\text{ox})} = 0.5$  (fractions of reduced and oxidized ends in the 2e-reduced species, and  $\tau_{(\text{red})} = \tau_{(\text{ox})}$  = lifetime of an electron in a given heteropoly end.<sup>12</sup> For intramolecular first-order exchange,  $k = 1/\tau$ . The  $k$ 's range from  $2.0 \times 10^3 \text{ s}^{-1}$  at 300 K to  $1.8 \times 10^4 \text{ s}^{-1}$  at 340 K. Plotting  $\log(k/T)$  vs.  $1/T$  gives a straight line ( $r = 0.994$ ). Slope and intercept yield enthalpy and entropy of activation,  $\Delta H^\ddagger = 10.4 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -8.9 \text{ cal/mol K}$ .<sup>13</sup>

**Potentialities.** Uses for this easy method may be considerable. Rates may be brought within fairly broad appropriate ranges by varying temperature, bridges, bridged groups, substitutions (organic and/or heteropoly), and heteropoly blues, variously reduced by different potentials. Only one electron receptor need be heteropoly, containing only one NMR-active nucleus. Complexes like diamagnetic  $[\text{O}_{39}\text{W}_{11}\text{XCo}^{3+}\text{-pyrazine-MR}]^{-n}$  and their blues have been made<sup>1-3</sup> ( $\text{X}$  = various elements, MR = reducible heteropoly or other complex groups). Exchange rates too slow for line coalescence may be evaluated from line widths,<sup>6</sup> from magnetization transfer experiments, or from  $T_2$  measurements.<sup>12</sup> These interesting mixed-valence complexes involve one activation energy for through-bridge electron transfer and (an)-other(s) for electron hopping within the heteropoly blue portions.

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(11) Slow spin-lattice relaxation for P's close to the  $\text{Zn}_4$  layer ( $T_1 \approx 30 \text{ s}$ ) made signals from the other P's ( $T_1 \approx 9 \text{ s}$ ) more convenient for equilibrium constant calculations.

(12) In case of small line widths, where instrumental contributions to the error could be substantial, a Hahn spin-echo  $T_2$  measurement could provide a superior measurement of  $\tau$ .

(13) The magnitude of the negative value of the entropy of activation ( $-8.9 \text{ cal/mol K}$ ) is consistent with a nonadiabatic character of the intramolecular electron transfer inferred from the fact that the disproportionation constant has the statistical value and from the absence of electronic coupling between the two heteropoly portions of the complex. The electronic factor  $\kappa$  can be estimated,<sup>14</sup> from  $\Delta S^\ddagger = R \ln \kappa$ , to be  $1 \times 10^{-2}$ .

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## Inhibition of the Hydrolysis of *p*-(Dimethylamino)benzoyl Fluoride by Potassium Fluoride<sup>1</sup>

Byeong Doo Song and William P. Jencks\*

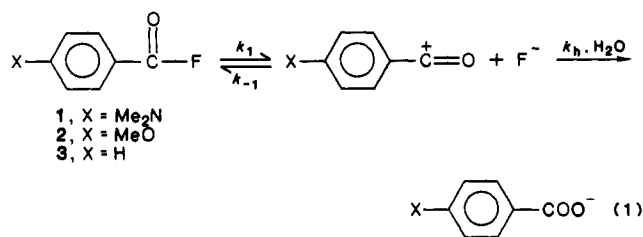
Contribution No. 1612

Graduate Department of Biochemistry, Brandeis University  
Waltham, Massachusetts 02254

Received February 9, 1987

Previous reports<sup>2-4</sup> of the rate-enhancing effect of electron-donating substituents on the solvolysis of substituted benzoyl halides and the large sensitivity to solvent ionizing power (in highly polar solvents) of the solvolysis of acid halides with electron-donating substituents suggest that these reactions occur through acylium ion like transition states. For the hydrolysis of 2,4,6-trimethylbenzoyl chloride, a significant inhibition by tetra-*n*-butylammonium chloride was observed in 99% acetonitrile,<sup>3</sup> but little inhibition by chloride ion was observed in 95% acetone,<sup>5</sup> even though  $\rho$  is  $-3.9$  for the hydrolysis of 4-substituted 2,6-dimethylbenzoyl chlorides in 99% acetonitrile<sup>3</sup> and in 89.1% acetone.<sup>4</sup>

We report here inhibition of the hydrolysis of *p*-(dimethylamino)benzoyl fluoride in water by added potassium fluoride at constant ionic strength, which is expected for a common ion effect in a monomolecular solvolysis (eq 1). Figure 1 shows 50% inhibition by 2.0 M potassium fluoride of the hydrolysis of *p*-(dimethylamino)benzoyl fluoride<sup>6</sup> (1) and the theoretical curves for the observed rate constants, obtained from eq 2 with  $k_1 = 3.5 \times 10^{-3} \text{ s}^{-1}$  ( $3.3 \times 10^{-3} \text{ s}^{-1}$  in  $\text{D}_2\text{O}$ ) and  $k_{-1}/k_h = 0.6 \text{ M}^{-1}$ , based on the reaction scheme of eq 1.



In contrast, for *p*-anisoyl (2)<sup>6</sup> and benzoyl (3) fluorides, 1.0 M potassium fluoride *increases* the hydrolysis rate by 7.7- and 6.6-fold, respectively. The solvent deuterium isotope effect is  $k_{\text{HOH}}/k_{\text{DOD}} = 1.1$  for 1 and  $2.3 \pm 0.2$  for 2 and for 3 in the presence and in the absence of 1.0 M potassium fluoride.<sup>7</sup> This rate increase and the solvent isotope effect in the presence of fluoride ion for 2 and 3 suggest that fluoride ion and solvent both act as general base catalysts for nucleophilic attack of water on these acid fluorides.

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(7) The reaction was followed spectrophotometrically at 25 °C, ionic strength = 1.0, maintained with potassium chloride, and wavelength = 330 nm for 1, 275 nm for 2, and 240 nm for 3. The stock solution of potassium fluoride of  $\approx \text{pH } 6.0$  was prepared by addition of 2.96 N HCl (2.5 mL) to 4.0 M KF (200 mL); no buffer was added for the reaction. The hydrolysis of 1 is independent of the concentration of potassium phosphate, 50% dianion, up to 1.0 M. For 2 and 3, the same rate constant was observed in the absence of buffer and extrapolated to zero concentration of potassium phosphate, 50% dianion.