Registry No. OH^-, 14280-30-9; HF, 7664-39-3; $OH^-(H_2O)$, 23138-14-9; $OH^-(H_2O)_2$, 34118-36-0; $OH^-(H_2O)_3$, 34118-37-1.

Supplementary Material Available: Table of numerical values of experimental and theoretical rate constants shown in Figure 1 (1 page). Ordering information is given on any current masthead page.

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Nucleophilic Displacement as a Function of Hydration Number and Temperature: Rate Constants and Product Distributions for $OD^-(D_2O)_{0,1,2}$ + CH_3Cl at 200-500 K

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Nucleophilic displacement reactions which are exothermic do not react on every collision in the gas phase.[6,7] They exhibit a negative temperature dependence, rate constants *decreasing* with *increasing* temperature,[8] and reaction at 300 K is quenched dramatically by the addition of only one–three solvate molecules.[9] In each respect nucleophilic displacement differs from proton transfer, as contrasted in the companion paper.[10] Here we report how hydration influences the rate constant *and* the product distribution of the nucleophilic displacement reaction

$$OD^- + CH_3Cl = CH_3OD + Cl^- \qquad \Delta H^\circ = -50\ \text{kcal/mol}\,\text{[11]} \qquad (1)$$

within the temperature range 200–500 K. Such data invite interpretation using hypersurfaces calculated for hydrated reactants.[12]

Rate constants for reaction 1 have been measured with a selected ion flow tube (SIFT), using techniques similar to those used in the companion study.[10] Because the $OH^-(H_2O)$ reactant and the $^{35}Cl^-$ product have the same mass-to-charge ratio (m/e = 35), perdeuterated anions, produced from D_2O in the ion source, were used throughout. Rate constants, for the process $OD^-(D_2O)_n$ + CH_3Cl → products, were measured for the mono- and dihydrate (n = 1, 2) but were too small to measure for n = 3.[13] The data at 300 K agree, within ±30%, with data obtained by Bohme and colleagues using the flowing afterglow technique.[9]

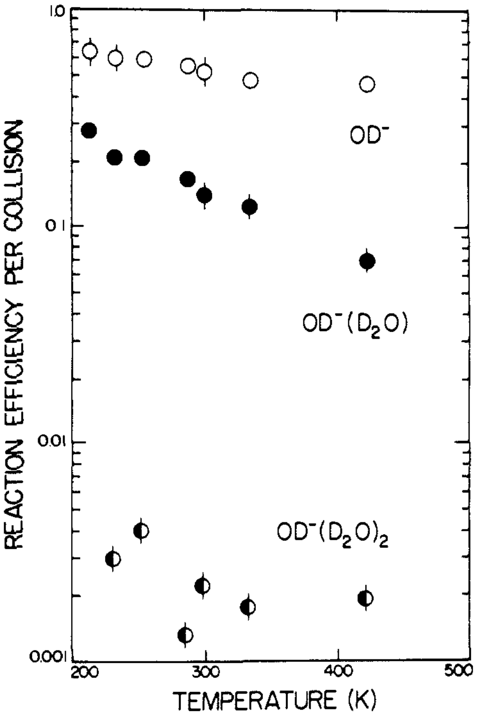

Figure 1. Reaction efficiencies for the reactions $OD^-(D_2O)_{0,1,2}$ + CH_3Cl as a function of temperature.

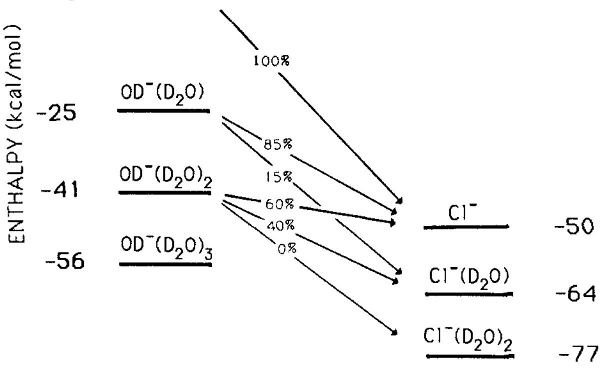

Figure 2. Ethalpy diagram for the reactants (left column) and products (right column), identified by the ionic species. Relative enthalpies are for undeuterated species[16] and yield reaction enthalpies by subtraction. Experimental product distributions (independent of temperature) are reported with error limits of ±3% for $OD^-(D_2O)$ and ±10% for $OD^-(D_2O)_2$.

Figure 1 shows the dependence of the rate constant on temperature and solvation number. What is represented is the *reaction efficiency*, which is the ratio of the experimental rate constant to a theoretical collision rate constant. Collision rate constants have been calculated by using the ACCSA procedure, developed by Clary.[13,14]

Reaction 1 shows the *negative* temperature dependence that has been shown experimentally[8] and has been predicted theoretically[15,8] for nucleophilic displacement at an sp^3 carbon atom.

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Hydrating the nucleophile with one water reduces the reaction efficiency,[9] but we show here that it *increases the negative temperature dependence*. Hydrating the nucleophile with two waters reduces the reaction efficiency by another 2 orders of magnitude,[9] but we show in Figure 1 that a similar negative temperature dependence is maintained.

The product distributions, reported in Figure 2, show that *Cl^- is the principal product*, whether the OD^- reactant has 0, 1, or 2 waters of hydration. Reactions efficiencies are approximately 50%, 10%, and 0.1%, respectively, to form Cl^- and 1% and 0.1% to form $Cl^-{\cdot}D_2O$[17] (Figure 1). The least exothermic channel is favored: strongly exothermic channels are avoided and, rather than follow them, there is no reaction at all. These systematic trends predict that *for the higher hydrates, solvation quenches reaction*, as confirmed experimentally. Similar trends have been established for both methyl bromide[18] and iodide.[19]

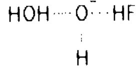
Three results require explanation: (1) Hydration reduces reactivity. (2) Hydration accentuates the negative temperature dependence of the reaction efficiency. (3) Hydrated reactants do not form hydrated products. These are discussed in turn.

(1) Wherever hydration of the reactant channels the reaction into a single product (Figure 2), hydration must progressively reduce the reaction exothermicity. If hydration decreases reactivity, this can then be expressed in terms of a reactivity/exothermicity relationship. The simplest of these is the Marcus relationship which has been applied successfully to nucleophilic displacement reactions in the gas phase *at a single temperature*.[20] This relationship describes *qualitatively*[21] the present result that, at any particular temperature, hydration reduces reactivity.

(2) Consider next how hydration affects the temperature dependence of the reaction efficiency. If hydration reduces the exothermicity (vide supra), how does the reduced exothermicity affect the temperature dependence? Analysis by Kebarle and colleagues[8] suggests that decreasing exothermicity should make the temperature dependence more negative[22] and data from a sequence of reactions of varying exothermicity demonstrate this trend.[8e] The results in Figure 2 exhibit this same trend: *hydration increases the negative temperature dependence of the reaction efficiency*.

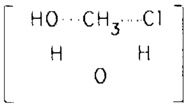
(3) The failure to form $Cl^-{\cdot}D_2O$ efficiently parallels our previous study on CH_3Br,[18] suggesting again[23] that the transition state (II)—energetically and entropically unfavorable—frustrates solvate transfer from nucleophile to leaving group.

In conclusion, nucleophilic displacement and proton transfer[10] are contrasted. First, proton transfer occurs on every collision (irrespective of temperature and hydration): nucleophilic displacement does not; and efficiencies decrease with increasing hydration and temperature. This kinetic behavior can be modeled with the double-minimum potentials used to describe the two reactions.[20d] Second, hydrated products are formed efficiently for proton transfer but not for nucleophilic displacement: progressive hydration quenches nucleophilic displacement but not proton transfer. In the transition state for proton transfer (I), the polar solvate lies at the center of charge (a low-energy pathway):[10] for nucleophilic displacement (II), the solvate must span the nucleophile and leaving group, as the charge travels down the molecular backbone (a higher energy pathway, entropically disfavored).[18]



$$HOH\cdots\underset{H}{O^-}\cdots HF$$

I



$$\left[\begin{array}{c} HO\cdots CH_3\cdots Cl \\ H \qquad H \\ O \end{array}\right]$$

II

Registry No. OH^-, 14280-30-9; CH_3Cl, 74-87-3; $OH^-(H_2O)$, 23138-14-9; $OH^-(H_2O)_2$, 34118-36-0.

Supplementary Material Available: Table of numerical values of experimental and theoretical rate constants used in Figure 1 (1 page). Ordering information is given on any current masthead page.

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(21) But not quantitatively.[20]

(22) The analysis considers how the reaction exothermicity affects the height of the central barrier in the double-minimum potential.[7,20] The temperature dependence becomes positive as the energy of the tip of the barrier exceeds that of the reactants.

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Polymetallic Systems with Subtle Spin Orders

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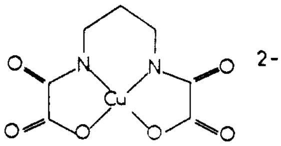
We have recently witnessed and been among the actors of a renaissance in molecular magnetism. One of the most important elements of this renaissance is the possibility of designing polymetallic systems exhibiting predictable magnetic properties.[1] Heteropolymetallic compounds play an important role along this line. Indeed, they offer a larger diversity than the homopolymetallic compounds, as for the exchange pathways between nearest-neighbor metal ions.[2-5] The goal of this paper is to emphasize that quite novel magnetic behaviors may be obtained in carefully designed polymetallic systems. For that, we present a few of the examples recently investigated in our group.

Some years ago, Monoyama et al.[6] described the copper(II) mononuclear dianion **1**, derived from the 1,3-propylenebis(oxamate) and noted here $[Cu(pba)]^{2-}$.



1

We have found that slow diffusion of aqueous solutions of $Na_2[Cu(pba)]$ and of $M(ClO_4)_2{\cdot}6H_2O$, M = Mn or Ni, affords the ordered bimetallic chains $MCu(pba){\cdot}nH_2O$. When M is manganese(II), the compound $MnCu(pba)(H_2O)_3{\cdot}2H_2O$ (**2**) was obtained in the form of well-shaped light-blue single crystals. The crystal structure was determined. **2** crystallizes in the orthorhombic system, space group *Pnma*. The lattice parameters are $a = 12.945$ (1) Å, $b = 21.250$ (4) Å, and $c = 5.2105$ (8) Å, with $Z = 4$ MnCu units. A perspective view of the structure is shown in Figure 1. The Mn^{2+} ions are in elongated octahedral surroundings with two water molecules in apical positions and the Cu^{2+} ions are in square-pyramidal surroundings with a water

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