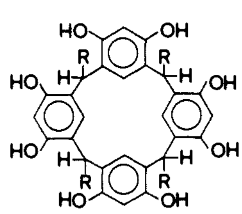
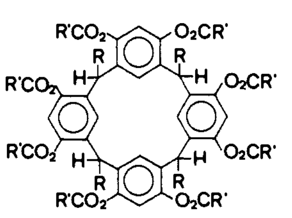
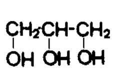


1a : R = $(CH_2)_{10}CH_3$
1b : R = CH_3
1c : R = C_6H_5

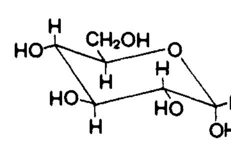


2a ; R = $(CH_2)_{10}CH_3$, R' = CH_3
2b : R = CH_3, R' = CH_3, C_2H_5
2c ; R = C_6H_5, R' = C_3H_7

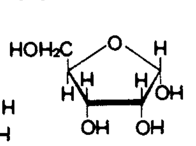


$\underset{OH}{CH_2}\underset{OH}{CH}\text{-}\underset{OH}{CH_2}$

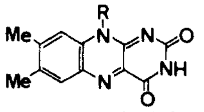
3



4 (α form)



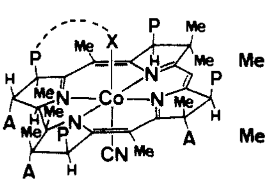
5 (α form)



6a : R = $CH_2\underset{OH}{(CH)_3}\underset{OH}{CH_2}$

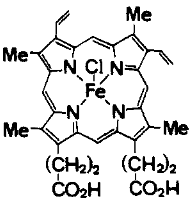
6b : R = $CH_2\underset{OAc}{(CH)_3}\underset{OAc}{CH_2}$

6c ; R = $(CH_2)_4CH_3$



A = CH_2CONH_2
P = $(CH_2)_2CONH_2$

7a : X = dimethylbenzimidazole ribonucleotide linked to P
7b : X = CN



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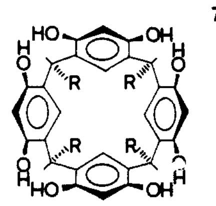

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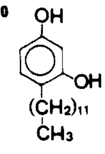

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aqueous (a) and organic (o) phases were such that could be correlated with the equation, $G_a + \mathbf{1a}_o \rightleftharpoons (G\text{-}\mathbf{1a})_o$; $K = [(G\text{-}\mathbf{1a})]_o/[G]_a[\mathbf{1a}]_o = 2.1 \times 10^2$ and 2.3×10^2 M^{-1} for **6a** (aqueous phase, 1 N HCl) and **7a**, respectively.[11] The maximal guest/host ratios of **6a**:**1a** ≅ 1:5 and **7a**:**1a** ≅ 1:2 were obtained by using aqueous solutions saturated with **6a** (in the order of 10^{-4} M) and **7a** (~1×10^{-2} M), respectively.[12] Hemin (**8**) as a solid could be solubilized slowly in benzene containing **1a**.

No solubilization of the guests (**3**–**8**) was observed when **2a** instead of **1a** was used as the host, indicating that the hydrogen bonding of the OH groups of **1a** with the polar groups of the guests, the OH groups in cases of **3**, **5**, and H_2O, is responsible for the present host–guest association. On the other hand, the imide moiety (CO–NH–CO) seems to be primarily responsible for the binding of **6a**, since **6a** is rendered nonfluorescent[13] upon complex formation with **1a** and the benzene-soluble tetraacetate (**6b**)[13] and pentyl (**6c**)[14] derivatives also form stable complexes with **1a** in C_6H_6, as shown by fluorescence quenching. For **7a** the seven amide groups can be the sites of binding, since dicyanocobinamide (**7b**) is also bound with **1a**. The 4:1 stoichiometry for the complexes **3**–**1a** and H_2O–**1a** strongly suggests that a pair of hydrogen-bonded OH groups on adjacent benzene rings in **1a** provide the essential binding site; four such sites (refer to **9**) may independently interact with four molecules of small polar guests such as **3** and H_2O or may undergo multisite interaction with **5** and also with the four upward and three downward amide side chains of **7a** in a sandwich form as the 1:2 stoichiometry for **7a**–**1a** suggests. In fact, 4-dodecylresorcinol (**10**) (1.4×10^{-3} M in C_6H_6) which is unable to form such an OH pair fails to solubilize **3**–**8** to any detectable extent. It is also interesting to note that the complexes **3**–**1a** (4:1) and **7a**–**1a** (1:2) are monomeric as such in $CHCl_3$ as demonstrated by VPO.[15]

This study presents a novel example of polar substrate binding with macrocyclic polar hosts rendered soluble in apolar media. It is significant that the present polar host–guest interaction can compete favorably with the host–host, host–H_2O, and guest–H_2O interactions. These findings provide a basis for the elaborate molecular recognition of biological polar compounds and may also open a new synthetic chemistry thereof in apolar organic solvents.

Acknowledgment. This work was supported by a Grant-in-Aid for Special Projects from the Ministry of Education, Science, and Culture of Japan.

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(11) Monitored by electronic spectroscopy until equilibria were attained. Electronic spectra for species solubilized with **1a** in C_6H_6: **6a**, λ_{max} (ε) 382 (8.5×10^3), 452 (10.3×10^3), 477 nm (8.7×10^3); **7a**, 363 (28.1×10^3), 552 nm (8.4×10^3).

(12) In case of **6a** which has a very low solubility in water, the apparent ratio **6a**:**1a** may not necessarily be the stoichiometry.

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(15) Molecular weights are as follows: **3**–**1a**, 1497 (calcd for 4(**3**)·**1a**, 1474); **7a**–**1a**, 3678 (calcd for **7a**·2(**1a**), 3567).

The Distance Dependence of Intramolecular Electron-Transfer Rates: Importance of the Nuclear Factor

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Received August 31, 1987

The factors determining the distance dependence of intramolecular electron-transfer rates in small molecule systems[1-6] and metalloproteins[7-10] are of considerable current interest. In the semiclassical formalism[1,11] the rate constant k for intramolecular electron transfer is given by eq 1 where κ_{el} is the electronic

$$k = \kappa_{el}\nu_n\kappa_n \tag{1a}$$

$$\kappa_n = \exp\left[-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda RT}\right] \tag{1b}$$

$$\lambda = \lambda_{out} + \lambda_{in} \tag{1c}$$

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transmission coefficient, ν_n is a nuclear vibrational frequency, κ_n is the nuclear factor, λ_{out} is the solvent contribution to the reorganization barrier, λ_{in} is the contribution from the intramolecular modes, and ΔG° is the standard free-energy change for the electron transfer. In interpreting long-distance rates it is frequently assumed that the distance dependence arises entirely from the decrease in the electronic coupling H_{AB} of the redox sites with increasing separation. For nonadiabatic reactions ($\kappa_{el} \ll 1$) the product $\kappa_{el}\nu_n$ is given by[12]

$$\kappa_{el}\nu_n = 10^{13}\exp[-\beta(r - r_0)] \tag{2a}$$

where r_0 is defined so that the reaction is adiabatic (i.e., $\kappa_{el} = 1$) at $r = r_0$. In recent work[13] we have emphasized the significant role that the distance dependence of the nuclear factor can play, showing that the dependence of λ_{out} on distance (calculated from the dielectric continuum model[14,15]) can be quite large and should not be neglected in interpreting electron-transfer rates.[16] Here we show that this prediction is supported by experimental observations and that, for systems of the type $[M(NH_3)_5]_2$(bridge), the nuclear factor alone yields an exponential dependence of the rate constant on distance (eq 2b) with $\gamma \sim 0.9$ Å^{-1}.

$$\kappa_n = \kappa^\circ_n \exp(-\gamma r) \tag{2b}$$

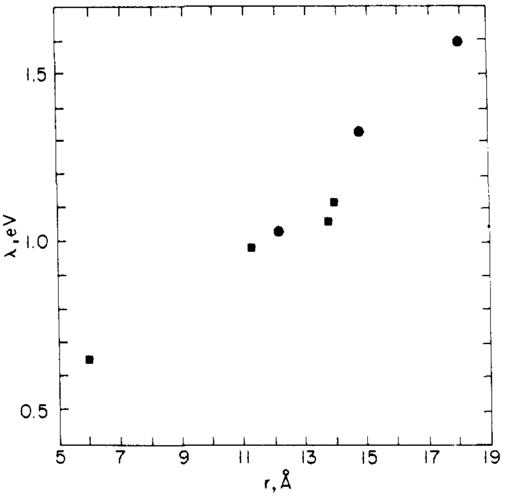

Figure 1. Distance dependence of the reorganization barrier. The squares are obtained from MMCT band maxima in water for symmetric mixed-valence $[Ru(NH_3)_5]_2L^{5+}$ ions where L = pyrimidine (6.0 Å), 4,4′-bipyridine (11.3 Å), 4,4′-bipyridylethylene (13.8 Å), and 4,4′-bipyridylacetylene (14.0 Å). The circles are obtained from ΔH^* for Os(II)-to-Ru(III) electron transfer in $(NH_3)_5$Os–iso(Pro)$_n$–Ru$(NH_3)_5^{4+}$ with n = (12.2 Å), n = 2 (14.8 Å), and n = 3 (18.1 Å).

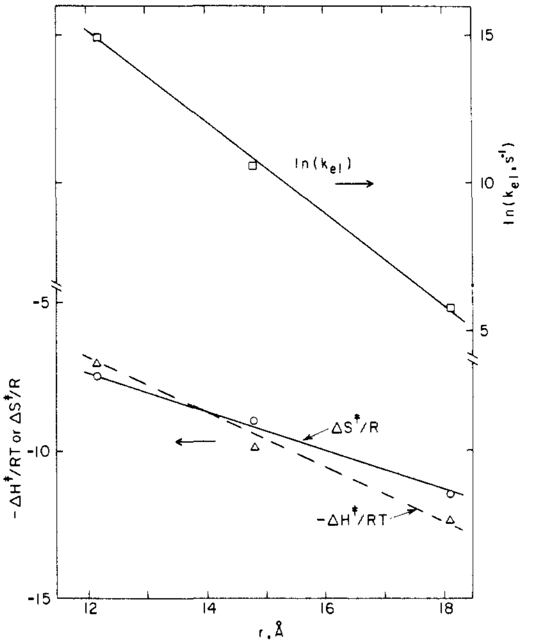

Figure 2. Distance dependence of the rate constants and activation parameters for intramolecular electron transfer in $(NH_3)_5Os^{II}$–iso-(Pro)$_n$–$Ru^{III}(NH_3)_5^{4+}$ with n = 1 (12.2 Å), n = 2 (14.8 Å), and n = 3 (18.1 Å), 0.1 M formate, pH ~ 3.

There are two experimental approaches to the evaluation of λ for intramolecular electron-transfer processes: (1) the determination of the energies of metal-to-metal charge-transfer (MMCT) transitions[17,18] and (2) the determination of ΔH^* for intramolecular electron transfer.[1] The MMCT band maximum E_{op} is comprised of λ, ΔG° (if the bridge is symmetric, ΔG° =

$$(NH_3)_5Ru^{II}(\text{bridge})Ru^{III}(NH_3)_5^{5+} \xrightarrow{h\nu = E_{op}} [(NH_3)_5Ru^{III}(\text{bridge})Ru^{II}(NH_3)_5^{5+}]^*$$

0), and ΔE_{ex} (if the transition observed is to an electronically excited state of the electronic isomer produced).[15,17-19] For

$$E_{op} = \lambda + \Delta G^\circ + \Delta E_{ex} \tag{3}$$

$[(NH_3)_5Ru]_2(\text{bridge})^{5+}$ complexes ΔE_{ex} is ~0.25 eV[19] because the most probable (intense) component of the MMCT envelope yields a spin-orbit excited state of Ru(III). When the activation parameters for the intramolecular electron-transfer rate constant are calculated from the transition-state expression, eq 4, λ contributes only to ΔH^* provided that the temperature dependence of the solvent's dielectric properties (bulk dielectric constant and refractive index) is negligible and that $\Delta S^\circ = 0$ (or that $|\Delta G^\circ| \ll \lambda$).[20,21] If $\Delta S^\circ = 0$, then

$$k = \frac{kT}{h}\exp\left(-\frac{\Delta H^*}{RT}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{4}$$

$$\Delta H^* \sim -RT \ln \kappa_n \tag{5a}$$

$$\Delta G^* \sim R \ln \kappa_{el} \tag{5b}$$

since $kT/h \sim 10^{13}$ s^{-1} at room temperature. The condition that $\Delta S^\circ \sim 0$ is met in the $(NH_3)_5Os^{II}$iso(Pro)$_n$Ru$^{III}(NH_3)_5^{4+}$ systems

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[12] When the redox sites are far apart, the electronic coupling between them will be weak, and the reaction will be nonadiabatic. Under these conditions the product $\kappa_{el}\nu_n$ is independent of ν_n and is given by[1,11]

$$\kappa_{el}\nu_n = \frac{2H_{AB}^2}{h}\left(\frac{\pi^3}{\lambda RT}\right)^{1/2}$$

The assumption that H_{AB}^2 decreases exponentially with distance leads to eq 2a.

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[16] (a) The intramolecular contribution λ_{in} is generally assumed to be independent of separation distance; ΔG° can depend on separation distance, depending on the nature of the system. (b) Taube[2] has discussed the expected correlation between H_{AB} determined from MMCT band intensities and ΔG^*. A correlation between the free energy of activation for intramolecular electron transfer and separation distance has been noted by Haim.[3]

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[21] Because the preexponential factor can be λ-dependent, ΔS^* can show a mild dependence on λ even when $|\Delta G^\circ| \ll \lambda$ or $\Delta S^\circ = 0$. For adiabatic electron transfers, the preexponential factor is the effective nuclear vibrational frequency ν_n which depends upon λ_{out} (and λ_{in}), while, for nonadiabatic electron transfers, the electronic factor depends inversely on the square root of λ.[12] The λ (and temperature) dependence of the preexponential factor is neglected here, as is the dependence of ΔG° on separation distance.

(iso = isonicotinyl, Pro = proline) for which $\Delta G^\circ \sim \Delta H^\circ \sim -0.15$ eV.[22]

Figure 1, a plot of λ versus metal–metal separation r, includes data for valence-trapped mixed-valence ions[18,23] $(NH_3)_5Ru^{II}$(bridge)$Ru^{III}(NH_3)_5{}^{5+}$ with bridge = pyrimidine (6.0 Å), 4,4′-bipyridine (11.3 Å), 4,4′-bipyridylethylene (13.8 Å), and 4,4′-bipyridylacetylene (14 Å) and for thermal electron transfer in $(NH_3)_5Os^{II}$(bridge)$Ru^{III}(NH_3)_5{}^{4+}$ with[21] bridge = iso(Pro)$_1$ (12.2 Å), iso(Pro)$_2$ (14.8 Å), and iso(Pro)$_3$ (18.1 Å).[24] In combining these data, the assumption is made that the inner-shell reorganization parameter λ_{in} is constant. Figure 1 then implies a good correlation between λ_{out} estimated from the energy of the intervalence band in the mixed-valence ions[25] and λ_{out} estimated from $\Delta H^\ddagger$ for intramolecular electron transfer in the polyproline systems.[26]

In Figure 2 the values of $\ln k$, $-\Delta H^\ddagger/RT$ ($\sim \ln \kappa_n$), and $\Delta S^\ddagger/R$ ($\sim \ln \kappa_{el}$) for the polyproline systems are plotted as a function of r. It is evident that, for these systems, the distance dependence of the nuclear factor (slope $\gamma = 0.91$ Å^{-1}) is *larger* than that of the electronic factor (slope $\beta = 0.68$ Å^{-1}). This is a very important result since it shows that the widely made assumption that the distance dependence of the rate constant arises solely from the distance dependence of the electronic factor can be in serious error. The results further show that measurements of the variation of the activation parameters with separation distance can provide invaluable information concerning the relative importance of the nuclear and electronic factors in determining the distance dependence of electron-transfer rates.[27]

Acknowledgment. We acknowledge helpful discussions with Drs. Bruce Brunschwig and Jay Winkler. The work done at Rutgers University was supported by the National Institutes of Health Grant GM 26324 and by the National Science Foundation Grant CHE 840552. S.I. is the recipient of a National Institutes of Health Career Development Award (AM 00734) (1980–1985) and a Camille and Henry Dreyfus Teacher Scholar Award (1981–1985). Research at Brookhaven National Laboratory was carried out under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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(24) (a) Internuclear distances for the polyproline complexes were estimated from computer-generated models by using the MOLECULAR EDITOR COMPILER program[24b] running on a Macintosh Plus microcomputer. The models were constructed by docking the relevant portions of the reported structures of *cis*-$[(NH_3)_4Ru(\text{isonicotinamide})_2](ClO_4)_3$,[24c] *trans*-poly-L-proline,[24d] and $[(NH_3)_5Co(\text{L-threonine})]Br_3$.[24e] The models were originally constructed for the Ru,Co system; it is assumed that the distances are also valid for the Os,Ru system. (b) Written by Rick Wargo and Allan Smith at Drexel University. Available through Kinko's Academic Courseware Exchange, 4141 State Street, Santa Barbara, CA 93110. (c) Richardson, D. E.; Walker, D. D.; Sutton, J. E.; Hodgson, K. O.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2216. (d) Burge, R. E.; Harrison, P. M.; McGavin, S. *Acta Crystallogr.* **1962**, *15*, 914. (e) Bagger, S.; Kristjänsson, I.; Søtofte, I.; Thorlacius, A. *Acta Chem. Scand. A* **1985**, *39*, 125.

(25) The experimental correlation between λ_{out} obtained from E_{op} with r was first noted by Powers et al. (Powers, M. J.; Salmon, D. J.; Callahan, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 6731).

(26) (a) λ_{out} should become independent of r at large r, and the apparent linear dependence of λ or r in Figure 1 is not expected to hold over a large range of separation distances. In addition to depending on the length of the bridging group, λ_{out} should also depend on its shape and composition. (b) Note that the conventional two-sphere model predicts at most a doubling in λ_{out} from its close-contact value to its value for infinite separation of the redox sites. Clearly λ_{out} changes by more than a factor of 2 for the systems considered in Figure 1. The increase in λ_{out} is also larger than predicted by an ellipsoidal cavity model. Specific interactions of the bridging group with the solvent might be partly responsible for this result.

(27) The distance dependence of λ_{out} has also been considered in a very recent paper (Geselowitz, D. A. *Inorg. Chem.* **1987**, *26*, 4135). Although a good correlation between free energies of activation for intramolecular electron transfer and E_{op} was found, such free-energy correlations must be interpreted with care since, as discussed above, experimental activation parameters are, in general, composite quantities.

A Two-Step Chemistry for Highlighting Heteroatom Species in Petroleum Materials Using ^{13}C NMR Spectroscopy

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Received May 18, 1987

A variety of characterization techniques have been reported for probing the type and distribution of heteroatom species in fossil fuel materials, usually coal and coal extracts. Often, a chemical transformation of the fossil fuel material has been used in combination with a suitable analysis technique in order to enhance the detection and identification of classes of heteroatom groups and to relate this information to aspects of the material's physical and chemical properties. These chemical reactions range from mild treatments including phase-transfer alkylation[1] to rather more severe treatments such as metal reductions[2] and oxidative degradation.[3]

Although these latter chemistries can provide information on heteroatom species which are normally unreactive to mild chemical treatments, the severity of these techniques reduces the selectivity for specific molecular types and greatly increases the probability for side reactions. Additional reaction products can also significantly complicate the already difficult task of characterizing fossil fuel materials.

In order to avoid some of the shortcomings inherent in one-step chemistries, we wish to report a two-step approach which combines an alkali metal reduction reaction with a phase transfer (PT) methylation reaction. A petroleum vacuum residuum (975 °F$^+$) has been chosen to demonstrate the application of this technique for highlighting heteroatom species, particularly sulfur species. Isotopically enriched methyl groups—93.1 mol% $^{13}CH_3I$ in all samples discussed here—are used as chemical "tags" in the second step of this process to facilitate the detection of reaction products in the residuum by high resolution ^{13}C NMR spectroscopy. The corresponding one-step products from these two chemical reactions are compared in Figure 1 to the sequential two-step product.

The aliphatic carbon region of the ^{13}C NMR spectrum for a virgin petroleum vacuum residuum is shown in Figure 1A. Although this residuum is known from elemental analyses to contain 5.89 wt % sulfur, 0.98 wt % nitrogen, and 0.67 wt % oxygen, there is little clear evidence from the NMR spectrum that molecules containing these heteroatoms are present in the sample.

Some heteroatom species, namely those which bear an exchangeable hydrogen in the virgin residuum, can be revealed by NMR techniques by using a phase-transfer methylation chemistry.[4] Acidic groups in the residuum (OH, NH, SH, and some CH) are converted to the corresponding methyl derivatives via deprotonation with an organic base and reaction of the resulting anion with an alkyl halide. Methyl iodide which is ^{13}C or ^{2}H isotopically labeled is customarily used in this reaction as the methylating agent if the products are to be characterized by NMR techniques.

The NMR spectrum of the PT-methylated residuum product is shown in Figure 1B and has been discussed in detail elsewhere.[5] One interesting observation is the presence of methyl resonances at 12.5 and 15.5 ppm in the PT-methylated product. These resonances have been assigned to thiomethyl ethers produced from mercaptans in the virgin residuum on the basis of their chemical shift values and our understanding of the PT methylation reaction.

It is clear from the relative intensities of hydrocarbon signals and of the highly isotopically enriched methyl groups that the

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