(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 ΔH^* for intramolecular electron transfer in the polyproline systems.[26]

In Figure 2 the values of ln k, $-\Delta H^*/RT$ ($\sim$ ln κ_n), and $\Delta S^*/R$ ($\sim$ ln κ_{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]

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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*-$[(NH_3)_4Ru(isonicotinamide)_2](ClO_4)_3$,[24c] *trans*-poly-L-proline,[24d] and $[(NH_3)_5Co(L\text{-}threonine)]Br_3$.[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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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 ^2H 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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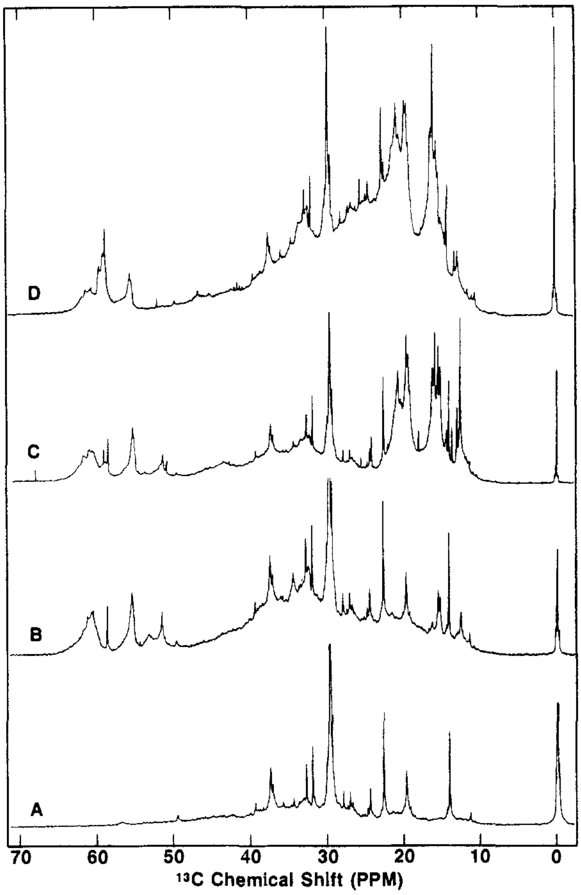

Figure 1. Aliphatic carbon region of the ^{13}C NMR spectrum for Figure 1: (A) petroleum vacuum residuum (975 °F$^+$ atmospheric equivalent of the vacuum distillation); (B) PT-methylated vacuum residuum; (C) reductively protonated, PT-methylated vacuum residuum; (D) reductively methylated vacuum residuum. Methyl iodide which was 93.1 mol% ^{13}C isotopically enriched was used in parts B through D. Each spectrum has been vertically adjusted to give about the same peak intensity for the methyl resonance terminating unbranched aliphatic chains at 14.1 ppm. The methylene signal at 29.7 ppm has been truncated in these spectra.

quantity of heteroatoms susceptible to this mild PT methylation chemistry is very low. In order to increase the concentration of heteroatoms highlighted by the NMR measurement, one option which has been used in previous studies[6] is to increase the severity of the chemistry.

One such chemistry, an alkali metal reduction using potassium metal in liquid ammonia, was completed on the petroleum residuum, and the NMR spectrum of this product is shown in Figure 1D. The reaction conditions were similar to those reported in ref 7. The reaction was quenched after 3 h with 93.1 mol% ^{13}C methyl iodide which is expected to trap most of the carbon and heteroatom anions produced in the reaction as the methyl derivative. Alkali metal reduction is known to attack and cleave a variety of weaker bonds in the hydrocarbon structure including the C–S bond in thiophene and benzothiophene structures.[8] Since the reaction is carried out in a hydrogen-donating solvent, hydrogenation of aromatic and some heteroaromatic ring systems is also a major product of this chemistry.

The aliphatic carbon region of the potassium reduced and methyl iodide quenched petroleum residuum is shown in Figure 1D. The increase in ^{13}C intensity from 10 to 40 ppm is consistent with the methyl products of both carbon and sulfur radicals generated during the metal reduction. Some evidence for methyl ethers of aliphatic alcohols also appears at 58 ppm as well as other oxygen–methyl resonances in the 50–65-ppm region common to those observed in Figure 1B.[9]

Unfortunately, it is difficult from this spectrum, especially in the 10–40-ppm region, to clearly differentiate those resonances which arise from carbon and from sulfur ring opening products since the methyl resonances associated with these reaction products do overlap in chemical shift position.

For this reason, an alternative approach involving two reaction steps was developed. In the first step, the petroleum residuum is reduced by using potassium metal in liquid ammonia as described above. Instead of quenching the reduction reaction with an alkyl halide, however, the reaction is quenched with ammonium chloride which protonates all reactive intermediates. The reductively protonated residuum is isolated as a stable product.[10,11]

In the second step, the reductively protonated residuum is methylated by using the PT methylation technique demonstrated in Figure 1B and described in ref 5. Since the reductively protonated products of hydrocarbon molecules are not sufficiently acidic to be deprotonated by the organic base in the second step, the two-step chemistry provides an unequivocal means to separate the spectral contributions from methyl groups associated with carbon and sulfur cleavage products. Sulfur species, arising from thiophene and benzothiophene type molecules, will be present as thiols at the conclusion of the first reaction step.

As expected, much of the broad resonance appearing from about 10–40 ppm in Figure 1D and assigned to methyl groups bonded to carbon has been eliminated from the spectrum of the two-step product (Figure 1C). Retained in this region of the spectrum, however, are three distinct bands at 12–15, 15–17.5, and 17.5–23 ppm which also appear in the spectrum of the reductively methylated product (Figure 1D).

From chemical shift data available on known materials, the upfield band is tentatively assigned to methyl products of aliphatic mercaptans. Methyl derivatives of aromatic mercaptans appear to resonate from about 15–23 ppm depending upon the degree of steric interaction experienced by the methyl group. Alkyl substitution on both aromatic ring positions ortho to the S–CH_3 group appears to be necessary to produce a methyl shift from 17.5 to 23.0 ppm. These assignments are consistent with the products anticipated from the reductive protonation of sulfur-containing molecules known to be present in petroleum distillates[12] and presumed to be present in residua.

The two-step chemistry in combination with high-resolution NMR spectroscopy provides a chemical approach to differentiate a subset of sulfur-containing molecules in a petroleum vacuum residuum. These results alone provide no conclusive information on the specificity of the reduction reaction for all benzothiophene type molecules in the residuum itself. Used for comparison purposes, however, this technique offers a unique opportunity to probe an important class of sulfur species in petroleum materials and to monitor the distribution of alkyl substitutions adjacent to these heteroatoms.

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(9) The absence of methyl intensity at 51 ppm—methyl esters of carboxylic acids—(compare 1D and 1B) suggests that the methyl iodide quench does not successfully trap all available groups in the residuum as a methylated product, an observation which has also been reported in coal studies (ref 2).

(10) Exactly 20.0 g of residuum in 220 mL of tetrahydrofuran was added to 14.0 g of potassium metal dissolved in 200 mL of liquid ammonia at −78 °C under a nitrogen atmosphere. After 3 h of reaction, 19.6 g of solid ammonium chloride was added to the reaction vessel, and the solution was allowed to gradually warm to ambient temperature. After the ammonia and tetrahydrofuran had evaporated, the product was dissolved in methylene chloride and vacuum filtered. The filtrates were evaporated to dryness in vacuo, and the residue was dried at 100 °C under vacuum to give 20.20 g (101.0% yield) of reductively protonated residuum.

(11) Although the carbon aromaticity of the reductively protonated residuum decreased from 30.0 to 22.1 mol% carbon, the ^{13}C NMR spectrum, which monitors the hydrocarbon skeleton, visually showed no evidence that reaction had occurred. The total sulfur content of this sample did decrease by 0.62 wt% S, presumably due to the reaction of benzyl alkyl sulfides and the elimination of sulfur from the sample as low molecular weight products.

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