C$_3$D$_8$ being noticeably different from, for example, neo-C$_5$D$_{12}$ and c-C$_4$D$_8$. The higher value for CD$_3$F than CD$_4$ in both cases is noteworthy since this reverses the trend found in alkanes of lower yield with higher bond dissociation energy; the reversal has been attributed in the nuclear recoil case to the difference in structure between planar CH$_3$ and nonplanar CF$_3$ groups, and consequent accompanying differences in residual excitation following the fast abstraction reaction.[6]

Absolute measurements of yield are not feasible in our experiment.[11] However, hot yields (presumably mostly of the abstraction product[11]) as high as 31% have been found for 3-eV H* or D* reactions with hydrocarbons,[12-15] while abstraction yields of 20-40% are found in experiments with hot tritium atoms from nuclear recoil.[8] Detailed quantitative comparison of the two kinds of experiments would require knowledge of the energy losses in the nonreactive collisions of tritium with each molecule of the mixture over the whole possible energy range. Within the semiquantitative range of present estimates, the magnitude of the DT yield variations in the photochemical experiments is sufficient to account for much of the corresponding variation found in nuclear recoil experiments. The photochemical experiments imply that low energy (<3 eV) abstraction reactions comprise an appreciable part of the observed nuclear recoil abstraction yields, and are consistent with the "energy cut-off" model for such reactions.

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Cation-Induced Linkage Isomerism of the Thiocyanatopentacyanocobaltate(III) Complex

Sir:

The mode of bonding of the ambidentate ligand thiocyanate to transition metals has been shown to be subject to a variety of influences; these include the nature of the metal,[1-3] the steric and electronic characteristics of other ligands in the coordination sphere,[1,4-6] and the nature of the solvent.[7] In a recent report a noncoordinated anion was shown to influence the mode of bonding in [Pd(Et$_4$dien)NCS]$^+$.[8] We now wish to report that for the complex Co(CN)$_5$SCN^{3-} the

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nature of the countercation determines which of the two linkage isomers is the more stable in solid materials.

The complex K$_3$[Co(CN)$_5$SCN] was first prepared several years ago and shown to be stable to isomerization in the solid state.[9] More recently, the linkage isomer K$_3$[Co(CN)$_5$NCS] has been reported.[10] We have converted each of these compounds to a tetra-n-butylammonium salt by extracting an aqueous solution of complex with a solution of [(n-C$_4$H$_9$)$_4$N]Cl in methylene chloride, evaporating the organic layer, and recrystallizing the residue from methylene chloride-ether. We have also converted K$_3$[Co(CN)$_5$SCN] to a tetra-n-butylammonium salt by preparing the acid H$_3$[Co(CN)$_5$SCN], titrating it to neutral pH with [(n-C$_4$H$_9$)$_4$N]OH, and removing the water under reduced pressure.

The crystalline (n-C$_4$H$_9$)$_4$N$^+$ salts prepared by the three pathways have identical electronic absorption spectra in aqueous solution (Table I) and identical

Table I. Electronic Spectra of Co(CN)$_5$NCS^{3-} and Co(CN)$_5$SCN^{3-} in Aqueous Solution

Compound	λ_{max}, nm	ϵ_{max}
[(n-C$_4$H$_9$)$_4$N]$_3$[Co(CN)$_5$NCS]	363	500
	265	2,350
	202	28,000
K$_3$[Co(CN)$_5$NCS]	363	447
	265	2,360
	203	24,000
K$_3$[Co(CN)$_5$SCN]	378	191
	265	17,100
	227	4,300
	200	16,700
K$_3$[Co(CN)$_5$CNS]^a	363	260
	263	13,800

^{a} Spectrum of the compound reported in ref 10. This may be interpreted as a spectrum of a mixture of about 70% K$_3$[Co(CN)$_5$SCN] and about 30% K$_3$[Co(CN)$_5$NCS].

infrared spectra in the C≡N stretching region (2140 cm^{-1}, s, br; 2113 cm^{-1}, vs) and may therefore be presumed to contain the same anionic linkage isomer. An unambiguous assignment of the mode of bonding in this compound is complicated by the presence of absorptions of (n-C$_4$H$_9$)$_4$N$^+$ in the region of the infrared spectrum where the C–S stretching band is expected and absorptions of the [Co^{III}(CN)$_5$] unit in the regions of the other thiocyanate fundamentals. However, a potassium salt, prepared by metathesis of the compound with KNCS in ethanol, shows an infrared absorption at 812 cm^{-1} assignable[1,2] to the C–S stretching mode of a nitrogen-bound thiocyanate; this potassium salt must then be the K$_3$[Co(CN)$_5$NCS] isomer. The electronic spectra of K$_3$[Co(CN)$_5$NCS] and the tetra-n-butylammonium salt are essentially the same and both are considerably different from the spectrum of K$_3$[Co(CN)$_5$SCN]. Thus the crystalline tetra-n-butylammonium salt must contain exclusively the isothiocyanatopentacyanocobaltate(III) anion, Co(CN)$_5$NCS^{3-}.[11]

In aqueous solution the linkage isomerization of either Co(CN)$_5$NCS^{3-} or Co(CN)$_5$SCN^{3-} is a relatively

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slow process. Electronic absorption spectra of aqueous solutions of the two isomers show only minor changes over a 24-hr period at 25°. It is also interesting that $Co(CN)_6{}^{3-}$ does not appear to affect significantly the isomerization rates; in an aqueous solution 0.001 M in complex and ca. 0.0005 M in $Co(CN)_5{}^{3-}$, the only spectral changes noted after 2 hr could be attributed to the expected[12] Co(II)-catalyzed formation of Co-$(CN)_6{}^{3-}$. A comparison of the molar extinction coefficients reported here for the electronic absorption spectrum of $K_3[Co(CN)_5NCS]$ with those reported by Stotz, Wilmarth, and Haim[10] indicates that their compound, formed by the direct substitution of NCS^- into $Co(CN)_5H_2O^{2-}$, is a mixture of about 70% $Co(CN)_5$-SCN^{3-} and about 30% $Co(CN)_5NCS^{3-}$. This conclusion is supported by cyclic voltammetric studies which show distinctly different electrochemical behavior for $Co(CN)_5SCN^{3-}$ and $Co(CN)_5NCS^{3-}$, whereas the product prepared by the substitution procedure[10] gives overlapping waves which indicate that both isomers are present.[13,14]

It has been reported that $K_3[Co(CN)_5NCS]$ isomerizes to $K_3[Co(CN)_5SCN]$ on heating.[10] The thermogram of a sample of $K_3[Co(CN)_5NCS]$ prepared by our procedure shows two irreversible endotherms between 25 and 200°. The infrared spectra of KBr pellets of the original compound and of a sample which had been heated to 100° (before the onset of the first endotherm) are identical. Infrared spectra of samples heated to 140° (before the onset of the second endotherm) and to 200° (after the second endotherm) are identical with each other and with the spectrum of $K_3[Co(CN)_5SCN]$. In addition, the electronic spectrum of a sample heated to 200° is identical with that of $K_3[Co(CN)_5SCN]$. The peak at 128° thus represents a phase transition associated with the isomerization of $K_3[Co(CN)_5NCS]$ to $K_3[Co(CN)_5SCN]$. This is not a reversible transition, and we conclude that $K_3[Co(CN)_5SCN]$ is more stable than $K_3[Co(CN)_5NCS]$ in solid samples.[15]

In contrast to the situation with K^+ as counterion, it is apparently not possible at 25° to prepare a pure sample of $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5SCN]$. A precipitate that contains mainly $[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5SCN]$ can be obtained by concentrating an aqueous solution at 0°; this material completely isomerizes to $[(n\text{-}C_4H_9)_4N]_3$-$[Co(CN)_5NCS]$ at room temperature within 3 days. It is also possible by rapid evaporation of a fresh (n-$C_4H_9)_4N^+$–CH_2Cl_2 extract of $Co(CN)_5SCN^{3-}$ to obtain an oily residue that contains mainly the S-bonded isomer; however, no S-bonded isomer is left after the oily material is crystallized.

The role the countercation plays in the isomerization

is of considerable interest. We suggest that the stabilization of the N-bonded isomer is due to an electronic effect in which the polarizable end of $-NCS^-$ is better accommodated by the nonpolar, hydrocarbon environment of the (n-$C_4H_9)_4N^+$ counterion. We further suggest that the stabilization of the S-bonded form in the compound containing K^+ as counterion is due to favorable interaction with the hard end of coordinated $-SCN^-$.[16] We are hopeful that the counterion stabilization feature, which allowed us to prepare materials containing exclusively the Co-$(CN)_5NCS^{3-}$ isomer, will have further synthetic utility in this field.

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(16) A similar interpretation could be put forward to explain the observed[14] solvent effect on the relative stabilities of the two isomers.

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Kinetic Isotope Effects on the (2 + 2) Cycloadditions of Diphenylketene with α- and β-Deuteriostyrene

Sir:

Secondary deuterium isotope effects on Diels–Alder reactions and on radical additions to olefins are small and inverse ($k_H/k_D < 1$),[1-5] in accord with theoretical expectations for a partial change in hybridization of the reactant carbons from sp^2 toward sp^3 in the transition-state region.[6,7] In radical additions, the olefinic carbon becoming the new radical center shows no secondary deuterium isotope effect;[2-5] it retains a nominal sp^2 hybridization throughout the addition.

One might anticipate, then, that a one-step (2 + 2) cycloaddition would be characterized by inverse secondary deuterium isotope effects at each terminus of an olefinic reactant; the inequality of the two inverse isotope effects would provide a measure of asymmetry in the transition state.[8] A two-step mechanism would give an inverse kinetic isotope effect at the center first bonded to the other reactant and no effect at the adjacent carbon. Thus the distinction between an asymmetric one-step and authentic two-step mechanism would depend on accurate determinations of both kinetic isotope effects and, possibly, on a value judgment between "small" and "negligible" deviations below 1.0 of k_H/k_D.

A kinetic investigation of the reactions between diphenylketene and mixtures of styrene with α-deuterio- or β,β-dideuteriostyrene shows this logical prognosis to be markedly erroneous. The kinetic isotope effect

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(15) In the thermogram of $K_3[Co(CN)_5SCN]$ there is an irreversible endotherm at about 150°. Infrared spectra of the original compound and the heated sample are identical. This peak may represent the loss of the small amount of solvent which the elemental analysis indicates is present.

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