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 $Co(CN)_5{}^{3-}$ 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% $Co(CN)_5SCN^{3-}$ 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 $(n\text{-}C_4H_9)_4N^+$–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 $(n\text{-}C_4H_9)_4N^+$ 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.

Acknowledgment. We thank the National Science Foundation for support of this research.

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[14] We have allowed aqueous solutions containing pure samples of each of the linkage isomers to come to equilibrium. At 40°, the position of equilibrium as measured from electronic absorption spectra corresponds to about two times as much $Co(CN)_5SCN^{3-}$ as $Co(CN)_5NCS^{3-}$. Thus our results indicate that the product formed[10] by the NCS^- substitution into $Co(CN)_5H_2O^{2-}$ at 40° is essentially the appropriate equilibrium mixture for the given conditions. It is also of interest that in CH_2Cl_2 at 40° the equilibrium position is far to the side of the $Co(CN)_5NCS^{3-}$ isomer and is reached starting from $Co(CN)_5SCN^{3-}$ in about 4 hr.

[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.

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

Diane F. Gutterman, Harry B. Gray
Contribution No. 3813, The Arthur Amos Noyes Laboratory of
Chemical Physics, California Institute of Technology
Pasadena, California 91109

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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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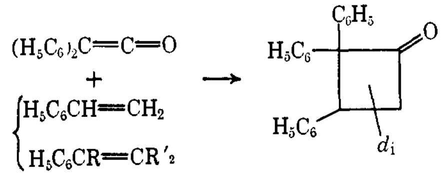
k_H/k_D at 65° per deuterium at the β position of styrene determined through intermolecular competition experiments is 0.91—an inverse effect, as expected; but k_H/k_D for substitution at the α position is 1.23!



R,R' = D, H or H, D

The kinetic isotope effects determined in a series of runs are given in Table I.

Table I. Secondary Deuterium Isotope Effects in (2 + 2) Cycloadditions between Diphenylketene and Deuteriostyrenes at 65°

Sample	Run	Molar ratio, styrene/ketene	k_H/k_D Mass spec	k_H/k_D 100-MHz nmr
$H_5C_6CD{=}CH_2$	1	1.70	1.213	1.254
	2	2.86	1.234	1.221
	3	4.01	1.250	*a*
	4	4.37	1.231	1.208
		Av	1.235	1.227
$H_5C_6CH{=}CHD$[b]	5	1.59	0.920	0.936
	6	2.34	0.913	0.899
	7	2.95	0.904	0.903
	8	4.50	0.896	0.902
		Av	0.908	0.910

[a] Insufficient sample for nmr spectrum. [b] Reaction run with β,β-dideuteriostyrene, and k_H/k_D calculated on a per deuterium basis.

Such a substantial normal isotope effect has become associated with the twisting of an sp^2 carbon out of conjugation with an adjacent p orbital as a necessary prelude to bonding with another atom. Such normal isotope effects have usually been observed or interpreted as intramolecular secondary deuterium isotope effects on a product-determining rather than a rate-determining portion of a reaction profile.[9,10]

Excess diphenylketene and styrene give a practically quantitative yield of adduct; with *cis*-β-deuteriostyrene, the addition is fully stereoselective *cis* on the double bond.[11] Thus the observed k_H/k_D of 1.23 may not be rationalized as arising from an intramolecular competition between ring closure and some other process following the rate-determining formation of a single bond and a difunctional intermediate.

The large isotope effects observed in the addition of diphenylketene with styrene imply a significant progress toward bond making at both α and β positions of styrene in the rate-determining activated complex. At the β carbon, the hybridization change sp^2 → sp^3 is in progress as a new bond is formed between ketene and olefin. At the α carbon, the transition state has a weaker C-H bond than the ground state, so that $\Sigma_i(\bar{\nu}_i(H) - \bar{\nu}_i(H)^{\pm})$ is positive and $k_H/k_D > 1$.[6,7]

The orbital symmetry prohibition against a concerted thermal *cis,cis* addition between an olefin and two parallel p orbitals on the C=C bond of the ketene[12] is thus reflected in an asymmetrical transition state characterized not by different extents of the same process but by different modes of approach toward bond making, manifested in contrary secondary deuterium kinetic isotope effects at the two termini of styrene.

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[14] National Science Foundation Predoctoral Trainee, 1965–1968.

John E. Baldwin,[13] Jon A. Kapecki[14]
Department of Chemistry and Chemical Engineering
University of Illinois, Urbana, Illinois 61801

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Asymmetric Induction in an Outer-Sphere Redox Reaction

Sir:

The experimental observations which we report here bear on two questions important to the theoretical interpretation of redox reactions of the outer-sphere type.[1] These questions are how close together the reactants must approach in order for the electron to be transferred and whether there is any preferred relative orientation of the reactants. In general, theoretical treatments of this type of electron-transfer reaction assume the reactants to have spherical symmetry.[2]

The reaction which we have chosen for study is a classic example of the outer-sphere reaction (phen = 1,10-phenanthroline)

$$\mathrm{Co(phen)_3}^{3+} + \mathrm{Cr(phen)_3}^{2+} \longrightarrow \mathrm{Co(phen)_3}^{2+} + \mathrm{Cr(phen)_3}^{3+} \quad (1)$$

As is usual with Co(III)–Cr(II) reactions, reaction 1 is very much more rapid than substitution on either Co(III) or Cr(III). When a solution 5×10^{-3} *M* in $CrCl_2$ and 1.5×10^{-2} *M* in 1,10-phenanthroline is mixed with a slight excess of a solution 5×10^{-3} *M* in $Co(phen)_3Cl_3$, the main net change which is observed is the reaction of eq 1.

We have resolved the optical isomers of $Co(phen)_3{}^{3+}$ by the method of Lee, Gorton, Neumann, and Hunt.[3] When *l*-$Co(phen)_3{}^{3+}$ is used to oxidize $Cr(phen)_3{}^{2+}$, the product solution is dextrorotatory, and when *d*-$Co(phen)_3{}^{3+}$ is the oxidizing agent, the product solution is levorotatory, rotations being measured at the sodium D line. Optical rotatory dispersion curves have been obtained for both isomers of $Co(phen)_3{}^{3+}$ and for the solutions resulting from the oxidation of $Cr(phen)_3{}^{2+}$ by optically active $Co(phen)_3{}^{3+}$. Solutions of *d*-$Co(phen)_3{}^{3+}$ are strongly dextrorotatory in the region 400–450 mμ. The product solution from the oxidation of $Cr(phen)_3{}^{2+}$ by *d*-$Co(phen)_3{}^{3+}$ is strongly levorotatory in this same region. That the change in the sign of rotation during the reaction is due to the formation of an optically active Cr(III) complex was substantiated by separation of the species in the product solution on

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