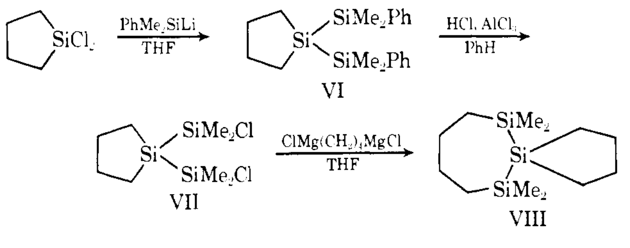
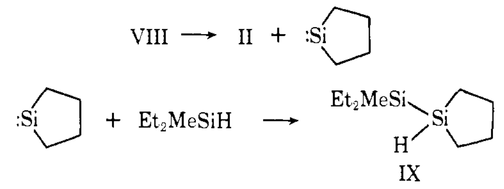
in the presence of aluminum chloride in benzene. Then, a tetrahydrofuran solution of VII was treated with tetramethylene di-Grignard reagent and this gave 5,6,11-trisilaspiro-4,6-undecane (VIII) as an oil (bp 97–98° (1 mm)). The assigned structure is in accord with spectral data of VIII: mass spectrum M^+ 256; nmr a singlet at δ 0.11 (12 H, SiMe), two multiplets at 0.77 (8 H, $SiCH_2C$) and 1.59 (8 H, CCH_2C); uv (in *n*-hexane) 219 nm (ϵ 8700).



Irradiation of an *n*-hexane solution of VIII containing a 10 molar excess amount of diethylmethylsilane as a trapping agent by a 160-W low-pressure mercury arc lamp for 20 hr afforded II and a new product, the yield of II being 80–90%. The latter product was isolated by preparative vpc and its structure was elucidated to be IX from its nmr spectrum: a singlet at δ 0.06 (3 H, SiMe), multiplets at 0.50–1.10 (14 H, SiEt, $SiCH_2C$), and at 1.58 (4 H, CCH_2C), and a quintet at 3.60 (J = 4.6 Hz, 1 H, SiH). The disilane IX should arise from the insertion of the cyclic silylene to the Si–H bond of diethylmethylsilane. Thus, the cyclic silylene was found to undergo normal insertion reaction into a silicon–hydrogen bond like the dimethylsilylene.



Related works are in progress and will be reported elsewhere.

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Some Unusual Anion Effects on the Rate of Reduction of Iron(III) Complexes[1]

Sir:

Electron transfer to the iron atom in cytochrome c can occur either directly or *via* the edge of the porphyrin ring system.[2,3] Electron transfer to the iron atom *via* the tyrosine residues of the polypeptide chain has also been proposed.[4,5] In an attempt to distinguish between these pathways, we are studying the effect of anions on the rate of reduction of cytochrome c^{III} by chromium(II).[6] In the course of this work, we observed that the reduction of cytochrome c^{III} by chromium(II) is markedly catalyzed by thiocyanate ions under conditions where chloride ions have a negligible effect. We now wish to report the results of a study of the effect of anions on the rate of reduction of the tris(1,10-phenanthroline) and the tris(2,2′-bipyridine) complexes of iron(III) by ferrous ions (eq 1). These effects are compared with those previously observed on the Fe^{3+}–Fe^{2+} reaction (eq 2).

$$Fe(phen)_3{}^{3+} + Fe^{2+} \longrightarrow Fe(phen)_3{}^{2+} + Fe^{3+} \qquad (1)$$

$$Fe^{3+} + Fe^{2+} \rightleftharpoons Fe^{2+} + Fe^{3+} \qquad (2)$$

The oxidation–reduction reactions were studied on the stopped-flow apparatus previously described.[7] The kinetics of the reactions were determined under pseudo-first-order conditions, with the ferrous ions present in excess. In most of the runs the formation of the iron(II) complex was followed at its absorption maximum in the visible region of the spectrum (510–529 nm); in some instances, the disappearance of the iron(III) complex was also followed (591–617 nm). Except where noted, the reactions were studied in 1.0 *M* perchloric acid at 25.0°.

Values of k_0 and of k_1 defined by eq 3 and 4 (where X^- represents the added anion) are presented in Table I, which also contains data on the effect of anions on the reduction of Fe^{3+} by Fe^{2+} ions. It is evident from the rate constants presented in this table that

Table I. Comparison of the Effect of Anions on the Reduction of Iron(III) Complexes by Ferrous Ions in 1.0 *M* Perchloric Acid at 25.0°

Iron(III) complex	X^-	k_0, M^{-1} sec^{-1}	k_1, M^{-2} sec^{-1}	Ref
$Fe(phen)_3{}^{3+}$		3.40×10^4		*a*
$Fe(phen)_3{}^{3+}$	Cl^-		4.9×10^5	*a*
$Fe(phen)_3{}^{3+}$	Br^-		3.8×10^5	*a*
$Fe(phen)_3{}^{3+}$	I^-		2.4×10^8	*a*
$Fe(phen)_3{}^{3+}$	$N_3{}^-$		8.1×10^8	*a, b*
$Fe(phen)_3{}^{3+}$	SCN^-		2.0×10^9	*a*
$Fe(bipy)_3{}^{3+}$		1.88×10^4		*a*
$Fe(bipy)_3{}^{3+}$	Cl^-		2.9×10^5	*a*
$Fe(bipy)_3{}^{3+}$	SCN^-		8.9×10^8	*a*
$Fe(dimbipy)_3{}^{3+\,c}$		0.032×10^4		*a*
$Fe(dimbipy)_3{}^{3+\,c}$	Cl^-		7.4×10^3	*a*
$Fe(dimbipy)_3{}^{3+\,c}$	SCN^-		3.8×10^7	*a*
Fe^{3+}		3.0		*d, e*
Fe^{3+}	Cl^-		87	*d, e, f*
Fe^{3+}	$N_3{}^-$		7.1×10^7	*d, g*
Fe^{3+}	SCN^-		2.4×10^3	*d, f, h*

[a] This work. [b] Medium was a 1 *M* NaN_3–$NaClO_4$–$HClO_4$ mixture. [c] The ligand is 4,4′-dimethyl-2,2′-bipyridine. [d] Ionic strength = 0.55 *M*, temperature = 20°. [e] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [f] This reaction proceeds by parallel inner- and outer-sphere paths. [g] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961). [h] R. A. Horne, Ph.D. Thesis, Columbia University, 1955.

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$$d[Fe(phen)_3^{2+}]/dt = k_{obsd}[Fe(phen)_3^{3+}][Fe^{2+}] \qquad (3)$$

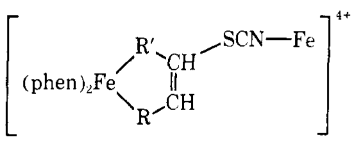
$$k_{obsd} = k_0 + k_1(X^-) + k_2(X^-)^2 + \ldots \qquad (4)$$

added anions have very different effects on the rates of the $Fe(phen)_3^{3+}$–Fe^{2+} and Fe^{3+}–Fe^{2+} reactions.[8] In particular, added thiocyanate has a much larger effect on the former reaction than on the latter. Moreover, the ratio of k_1 for azide compared to thiocyanate is only 0.4 for the $Fe(phen)_3^{3+}$–Fe^{2+} reaction, while this ratio is 3×10^4 for the Fe^{3+}–Fe^{2+} reaction. Spectrophotometric and kinetic analysis of the reaction products showed that $FeNCS^{2+}$ is formed quantitatively in the thiocyanate-catalyzed $Fe(phen)_3^{3+}$–Fe^{2+} reaction.

The thiocyanate catalysis of the reduction of the phenanthroline and bipyridine complexes is undoubtedly due in part to the larger driving force for these reactions (because $FeNCS^{2+}$ is more stable than $FeNCS^+$). The magnitude of this factor may be estimated from the effect of thiocyanate on the reduction of Fe^{3+} by Fe^{2+}. The *outer-sphere* reduction of Fe^{3+} by $FeNCS^+$ proceeds about 30 times faster than the reduction of Fe^{3+} by Fe^{2+}.[9] Thus, if the reaction of $Fe(phen)_3^{3+}$ with Fe^{2+} ions were of a comparable weak-interaction, outer-sphere variety, we would expect the rate constant for the $Fe(phen)_3^{3+}$–$FeNCS^+$ reaction to be about 30 times larger than the rate constant for the $Fe(phen)_3^{3+}$–Fe^{2+} reaction. Evidently this is not the case, as may readily be ascertained by dividing k_1 for thiocyanate ($2.0 \times 10^9\ M^{-2}\ sec^{-1}$) by the stability constant of $FeNCS^+$ ($6.5\ M^{-1}$)[9] and comparing the second-order rate constant for the reaction between $Fe(phen)_3^{3+}$ and $FeNCS^+$ thus calculated with k_0 ($3.40 \times 10^4\ M^{-1}\ sec^{-1}$).[10–13]

The above considerations as well as comparisons with the effects of chloride, azide, and thiocyanate on reactions of known mechanism[14,15] strongly suggest that a new mechanism is operating in the thiocyanate (and azide and iodide) catalyzed reduction of the phenanthroline and bipyridine complexes. An attractive possibility is that the thiocyanate-catalyzed reaction proceeds *via* a bridged intermediate formed by nucleophilic attack of the sulfur atom of SCN^- on a carbon of the ligand ring system bearing a partial positive charge (eq 5).[16] These carbon atoms are presumably good sites for nucleophilic attack as a consequence of electron withdrawal by the central ferric ion. An alternative mechanism involves the addition of the thiocyanate (through the sulfur atom) to the π system of the ligand rather than addition to an electrophilic carbon atom. This type of addition can perhaps more readily account for the observation (Table I) that replacement of the hydrogen atoms in the 4 and 4′ positions of bipyridine by methyl groups does not significantly alter the value of k_1/k_0.

$$Fe(phen)_3^{3+} + SCN^- + Fe^{2+} \longrightarrow$$



(5)

Regardless of whether the oxidation–reduction reactions proceed by nucleophilic attack on a carbon atom or by π-complex formation (or some other mechanism), these studies show that added anions have very different effects on the rate of reduction of phenanthroline and bipyridine iron(III) complexes than they have on "ordinary" electron-transfer reactions. This difference in the reactivity patterns might be used to obtain information about the electron-transfer site in more complex systems. Thus the thiocyanate catalysis of the reduction of cytochrome c by chromous ions suggests that in this reaction the porphyrin ring system is the electron-transfer site. Similarly, the relatively large effect of thiocyanate on the rate of reduction of iron(III) and manganese(III) tetrapyridylporphines[17] raises the possibility that in this reaction, too, the electron-transfer site is the porphyrin ring rather than the central metal atom. These and related electron-transfer reactions are currently under active investigation in this laboratory.[18]

Acknowledgment. The authors wish to express their appreciation to Dr. Stanley Seltzer for helpful discussions.

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[8] The oxidation of free azide, iodide, or thiocyanate ions by the iron(III) complexes is sufficiently slow under the conditions used in these studies as not to interfere with the reduction of the iron(III) complexes by ferrous ions.

[9] T. J. Conocchioli and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 282 (1967).

[10] The ratio of k_1 for thiocyanate compared to chloride is also relatively small in other outer-sphere reactions. This ratio is only about 10 for the outer-sphere oxidation of Cr^{2+} by Fe^{3+} ions[11,12] and approximately 30 for the oxidation of U^{3+}.[13]

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[14] N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

[15] M. Orhanovic, H. N. Po, and N. Sutin, *J. Amer. Chem. Soc.*, **90**, 7224 (1968).

[16] Although the possibility of adjacent attack of the Fe^{2+} on the sulfur atom of the coordinated thiocyanate cannot be excluded, it is unlikely that this occurs to any significant extent under the conditions used in this work, since $FeNCS^{2+}$ is formed quantitatively in the reaction (and no $CrSCN^{2+}$ is formed in the reaction of $Fe(bipy)_3^{3+}$ with Cr^{2+} in the presence of thiocyanate).

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[18] Preliminary results indicate that the $Co(phen)_3^{3+}$–Fe^{2+} reaction is also catalyzed by added thiocyanate ions.

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Ground-State Substituent Effects. I. Deuterium and Methyl

Sir:

Theoretical interest has been directed toward the problem of substituent effects on cyclopropyl rings, especially those involved in Cope rearrangements.[1–3] Remarkably large displacements by substituents have been observed in norcaradiene–cycloheptatriene[4] and bullvalene[5] equilibria.[6] However, these systems are

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