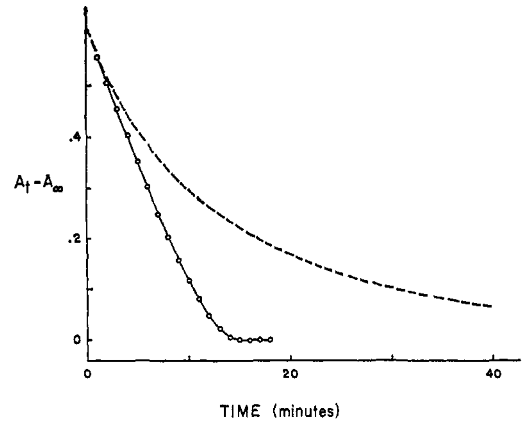

Figure 1. Absorbance change accompanying Co^{III} reduction: (—) observed for a reaction at 25° and 1.0 M ionic strength, where $[Co^{III}]_0 = 1.0 \times 10^{-3}$ M, $[Eu^{2+}]_0 = 2 \times 10^{-3}$ M, and $[H^+]_0 = 0.97$ M; (- - -) calculated for the same reaction according to the rate law $-d[Co^{III}]/dt = 0.83$ M^{-1} sec^{-1} $[Co^{III}][Eu^{2+}]$.

experimental error, this value was independent of $[H^+]$, $[Co^{III}]$, and $[Eu^{2+}]$.

In order to verify the form of the rate law for the isonicotinamide complex, rate eq 6 was integrated and used as the basis of a nonlinear least-squares program.[9] The program calculated the optimum value of each of the three independent parameters, k_1, k_2, and k_{-2}/k_3, which reproduce the absorbance–time data for each run. For the experiments involving the isonicotinamide complex, values ranged from 0.7 to 1.3 M^{-1} sec^{-1} for k_1, from 1.0 to 2.5 M^{-1} sec^{-1} for k_2, and from 0.01 to 0.07 for k_{-2}/k_3. In every case, satisfactory fits to the absorbance–time data were obtained.

Rate law 4 is consistent with the autocatalytic data obtained. There is, however, a great deal of uncertainty in the parameters. We observed in the course of these studies that the most marked deviations occurred in runs in which the $(Co^{III})/(Eu^{2+})$ ratio was low. Apparently some HL· may be lost to further reduction by Eu^{2+}. Our observation that free isonicotinamide is rapidly reduced by Eu^{2+} lends support to this suggestion.

Better values of k_1 and k_{-2}/k_3 can be obtained from the data by fixing the value of k_2 at 1.8 M^{-1} sec^{-1}, a value known from the previous experiments. With k_2 fixed at 1.8 M^{-1} sec^{-1}, values of $k_1 = 0.85 \pm 0.15$ M^{-1} sec^{-1} and $k_{-2}/k_3 = 0.011$–0.027 are found. The value of k_1 is in excellent agreement with that obtained from the initial slope of the second-order plots.

The reactions studied in this communication provide direct evidence for a radical-catalyzed electron-transfer mechanism. These observations also support the radical-intermediate mechanism for bridging ligands as proposed for Cr^{2+} reductions.[1] The rate of electron transfer to isonicotinamide will not be greatly affected by replacing H^+ with $(NH_3)_5Co^{III}$ since neither interacts with the π-acceptor orbitals of the aromatic ring. Thus, if electron transfer to the bridging ligand is the primary activation process for Co^{III} reduction, then the rate of Co^{III} reduction will be similar to and cannot greatly exceed the rate of electron transfer to the ligand.

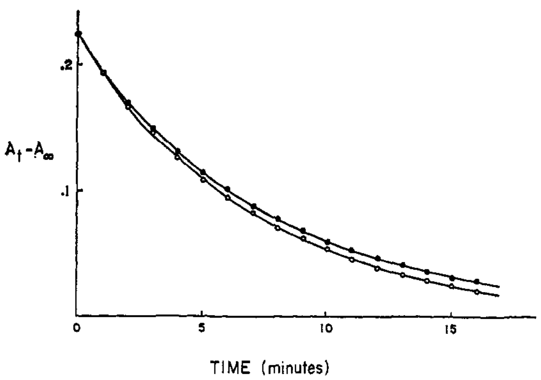

Figure 2. Eu^{3+} dependence of Co^{III} reduction. Reactions are at 25° and 1.0 M ionic strength, where $[Co^{III}]_0 = 2.0 \times 10^{-3}$ M, $[Eu^{2+}]_0 = 3.6 \times 10^{-4}$ M, and $[H^+]_0 = 0.88$ M: (○) no initial Eu^{3+}, (●) $[Eu^{3+}]_0 = 0.021$ M.

Such is the case in the present Eu^{2+} reductions. The similarity of the specific rate of Co^{III} reduction, 0.83 M^{-1} sec^{-1}, to the specific rate of electron transfer to HL^+, 1.8 M^{-1} sec^{-1}, indicates that isonicotinamide may act as a bridging ligand according to a radical-intermediate mechanism. This conclusion was reached for the Cr^{2+} reduction of complexes of this bridging ligand.[2] The similarity between Cr^{2+} and Eu^{2+}[10] is reasonable, since they have similar oxidation potentials and also share a tendency to exhibit inner-sphere paths.

Acknowledgment. This research was supported in part by the Center for Naval Analyses of the University of Rochester. Such support does not imply endorsement of the content by the U. S. Navy.

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(9) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 11, 431 (1963); IBM Share Program, SDA No. 3094, 1964.

(10) In spite of the similarity, an autocatalytic path is not observed for the corresponding Cr^{2+} reduction. The reason for this probably stems from the substitution-inert character of Cr^{III}. The analogous reaction for Cr^{2+} would be

$$Cr^{2+} + HL^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HL\cdot Cr^{III}$$

$$Co^{III} + HL\cdot Cr^{III} \xrightarrow{k_3} Co^{2+} + HLCr^{III}$$

Since Cr^{III} remains attached to HL·, return of the electron to Cr^{III} in a unimolecular decomposition would predominate over product formation by electron transfer to Co^{III} *via* a bimolecular process.

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Electron Transfer through Organic Structural Units. X. Catalysis, by Pyridine Derivatives, of Outer-Sphere Reductions of Cobalt(III). Evidence for an Unusually Reactive Outer-Sphere Reducing Agent

Sir:

The outer-sphere reductions, by Cr^{2+} or Eu^{2+}, of such slowly reacting oxidants as $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$ are dramatically accelerated by certain pyridine derivatives having a carbonyl or alkenyl substituent γ to nitrogen. Among catalysts acting in this manner are 4-pyridinecarboxylic acid, its carboxyl-bound $(H_2O)_5Cr^{III}$ derivative, and 1,2-bis(4-pyridyl)ethylene. The corresponding α derivatives have marginal catalytic action, and the β derivatives none. No such catalysis was observed with pyridine, 3-pyridinesulfonic acid, 4-cyanopyridine, 1,2-bis(4-pyridyl)ethane, or p-aminobenzoic acid. N-Alkylation of the pyridinecarboxylato catalysts enhances activity.

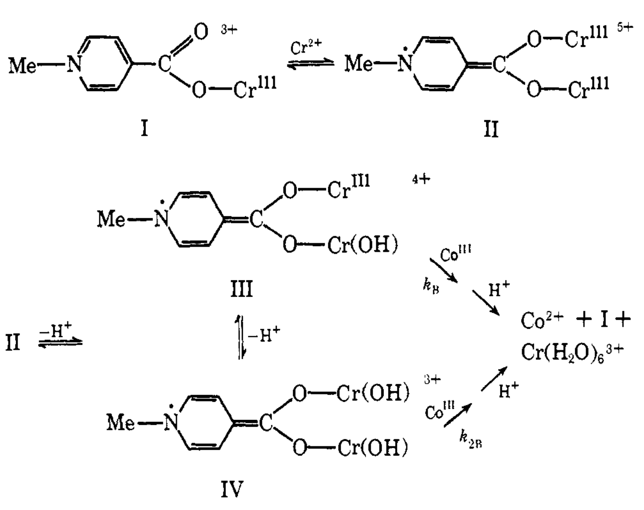
The kinetics of these catalyzed reductions are complicated by the gradual decrease of catalytic activity in reducing media, a difficulty that can be minimized at high concentrations of catalyst and low acidity. The outer-sphere[1] reductions of the $(NH_3)_6$, $(NH_3)_5py$, and $(NH_3)_5(DMF)$ complexes of Co^{III}, as catalyzed by the $(H_2O)_5Cr^{III}$ complex of *N*-methylpyridine-4-carboxylic acid (I) (generated *in situ* by inner-sphere reduction of the corresponding heterocyclic $(NH_3)_5Co^{III}$ complex[2]) conform to the rate law

$$\text{rate} = (Cr^{II})(Co^{III})(\text{cat})\left[\frac{k_{-1}}{(H^+)} + \frac{k_{-2}}{(H^+)^2}\right] \qquad (1)$$

Values of k_{-1} (M^{-1} sec^{-1} at 25°, $\mu = 1.0$) are 1.7 for $(NH_3)_6Co^{3+}$, 30 for $(NH_3)_5pyCo^{3+}$, and 37 for $(NH_3)_5(DMF)Co^{3+}$; values for k_{-2} (sec^{-1}) are 0.075 for $(NH_3)_6Co^{3+}$, 1.4 for $(NH_3)_5pyCo^{3+}$, and 0.96 for $(NH_3)_5(DMF)Co^{3+}$. At a catalyst concentration of 0.0018 *M*, the hexaammine complex, in 0.0084 *M* H^+, is reduced 26,000 times as rapidly as with catalyst absent; corresponding acceleration factors are 1000 for $(NH_3)_5pyCo^{3+}$ (in 0.033 *M* H^+) and 290 for $(NH_3)_5(DMF)Co^{3+}$ (in 0.050 *M* H^+). At catalyst concentrations of 10^{-5} *M* and pH values above 4, each of these reactions is, under our conditions, immeasurably rapid.[3] No inhibition by $Cr(H_2O)_6^{3+}$ is observed. Mixtures of Cr^{2+} and catalyst I exhibit no spectral irregularities indicative of a new species.

Our observations point to two active dinuclear radical cations, suggested here as III and IV,[4] formed at small steady-state concentrations in preequilibria (Scheme I). Since no negative deviation from first-order chromium(II) dependency is observed at high (Cr^{2+}), and since the catalyzed reductions of the Co^{III} complexes exhibit isosbestic points, it appears that the concentrations of radical ion II and, by implication, of its conjugate bases III and IV, lie well below that of catalyst I. If this be so, the reactivities of III and IV are truly remarkable, for although several orders of magnitude less concentrated than Cr^{2+}, they induce outer-sphere reductions of Co^{III} substrates at rates many thousand times those of the uncatalyzed reactions. Catalysis of the inner-sphere[1a] Cr(II) reductions of such rapidly reacting $(NH_3)_5Co^{III}$ complexes as the benzoato and acetato derivatives, although observable, is much less striking.

Scheme I



Treatment of 4-pyridinecarboxylic acid with zinc amalgam yields, first, a yellow (λ_{max} 460 nm), then a pink (λ_{max} 500 nm) species, neither of which reduces the Co^{III} complexes mentioned at an observable rate. Reductions by zinc may be assumed to proceed in two-electron steps, whereas the formation of the catalytically active species requires transfer of a single electron. Catalyzed reductions by Eu^{2+} probably proceed through odd-electron species analogous to III, which would not, however, be expected to remain bound to the substitution-labile Eu(III) formed in the initial electron-transfer step.[5]

Concerning the high reactivity of such radical cations as III and IV, we suggest that electron loss from an extended conjugated species requires much less bond distortion and solvent reorganization than from a small hydrated cation, a difference which, according to Marcus' picture,[6] should result in a more facile transfer. We are astonished, however, at the magnitude of the effect.[7]

Acknowledgments. Sponsorship of the Petroleum Research Fund, administered by the American Chemical Society, under Grant 2868-A3, is gratefully acknowledged. We thank Professor Francis Nordmeyer for

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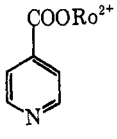
[1] (a) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969); (b) E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

[2] E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

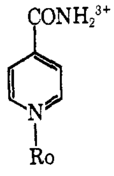
[3] Rate data from which eq 1 is derived were obtained for solutions in which $(H^+) = 0.008$–0.10 *M*, $(Cr^{II}) = 0.003$–0.04 *M*, $(Co^{III})_0 = 10^{-4}$–2×10^{-4} *M*, and $(\text{catalyst})_0 = 4 \times 10^{-4}$–$6 \times 10^{-3}$ *M*. When similar experiments were carried out with $(Co^{III})_0 > (\text{catalyst})_0$, serious depletion of catalytic activity was observed, and the apparent specific rate dropped drastically late in the course of the reaction. Evidence that complex I is indeed a catalyst, that is, that it is not consumed by the primary reaction, is obtained most directly from experiments with a deficiency of catalyst in biphthalate buffer. Under such conditions we find, for example, that more than 10 mol of $(NH_3)_5pyCo^{3+}$ is rapidly reduced for each mole of catalyst I taken.

[4] The intermediates proposed here are closely analogous to the stable free radicals prepared and characterized by E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964), and by E. M. Kosower and J. L. Cotter, *ibid.*, **86**, 5524 (1964). For kinetic studies of the reduction of organic substrates by such radicals, see, for example, M. Mohammed and E. M. Kosower, *ibid.*, **93**, 2709, 2713 (1971).

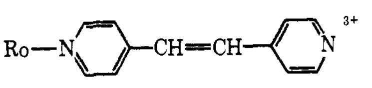
[5] There are several known instances in which a catalytically active species is produced in an electron-transfer reaction, which, under such circumstances, may become autocatalytic. Such autocatalysis has been observed in the Cr^{II} reduction of V at high pH (E. S. Gould and H. Taube, unpublished experiments, Stanford University, 1962), in the Eu^{II} reduction of VI [C. Norris and F. R. Nordmeyer, *J. Amer. Chem. Soc.*, **93**, 4044, (1971)], and in the Cr^{II} and Eu^{II} reductions of VII (E. Dockal and E. S. Gould, unpublished experiments, Kent State University, 1970).



V



VI



VII

Ro = "roseo" = $(NH_3)_5Co^{III}$

[6] See, for example, R. A. Marcus, *J. Chem. Phys.*, **24**, 970 (1956).

[7] A second unexpected feature of these reactions is their apparent sensitivity to the net charge on the reductant. Although no systematic study of the susceptibility of rates of Co^{III}–Cr^{II} reactions (either inner or outer sphere) to variations in charge of the reducing species have been reported, inner-sphere reactions of this type suffer only minor variation in rate on changing the charge type of the oxidant.[1a]

making known his experimental results before publication and Dr. William Movius for valuable discussions.

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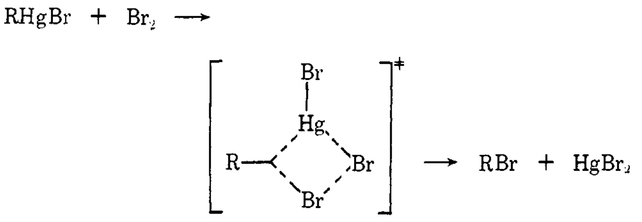
The Synthesis of Optically Active Organo Derivatives of Group IV Elements[1]

Sir:

Considerable evidence has accumulated indicating the electrophilic cleavages of organometallic compounds, in which vacant orbitals are available on the metal, occur with retention of configuration. For example, the electrophilic cleavage of organomercurials by bromine occurs with retention of configuration apparently through a closed transition state.[2] The observed re-



tention of configuration is forced by the mechanism. One method of investigating the stereochemistry of electrophilic substitution which occurs by an open transition state would be to use a system in which the metal has no low lying unfilled orbitals for complexation.

Reported here is the first general procedure for obtaining compounds of the type, R_3MR', M = Si, Ge, Sn, and Pb, where R′ is a simple alkyl group such as *sec*-butyl, containing an asymmetric carbon directly bonded to the metal atom. A single optically active derivative of a group IV element, [(−)-2,2-diphenyl-1-methylcyclopropyl]trimethyltin, has been reported.[3] However, this preparation was carried out by the unusual reaction of the trimethylstannyl anion with active 2,2-diphenyl-1-methylcyclopropyl bromide[4] and occurred with retention of configuration.

A well-known method for the preparation of unsymmetrical group IV organometallic compounds utilizes the reaction of triphenylmetal anions with alkyl halides.[5] This reaction has now been utilized to prepare optically active derivatives of the group IV metals.

Table I. Synthesis and Properties of Ph_3M(*sec*-butyl)

M	Conditions	$[\alpha]^{22}D$ obtained,[a] deg	$[M]^{22}D$ cor to opt purity,[b] deg	% yield[c]	Mp, °C	$[M]D$ calcd BR–MR,[d] deg	% inversion
Si	$Ph_3SiSiPh_3$, Li, THF, (*S*)-(+)-*sec*-butyl chloride, $[\alpha]^{22}D$ +5.43 (neat)	−1.23	−26.5	34	68–69.5	−51.5	51
Ge	Ph_3GeBr, Na, NH_3, (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−2.33	−34.6	39	71–71.8	−53.9	67
Sn	Ph_3SnCl, Na, DME,[e] (*S*)-(+)-*sec*-butyl chloride, $[\alpha]^{22}D$ +5.43 (neat)	−2.20	−61.0	46	70.5–71.5	−67.4	90
Sn	Ph_3SnCl, Na, DME,[e] (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−3.54	−59.3	55	70.5–71.5		88
Sn	Ph_3SnCl, Na, DME,[e] (*R*)-(−)-*sec*-butyl iodide, $[\alpha]^{27}D$ −26.8 (neat)	+9.39	+47.8	58	70.5–71.5	+67.4	71
Pb	Ph_3PbCl, Na, NH_3, ether, (*S*)-(+)-*sec*-butyl bromide, $[\alpha]^{22}D$ +8.31 (neat)	−4.16	−84.8	26	79.5–81	−126	67.5

[a] (*c* 5–8 *M*, benzene). [b] The specific rotations of optically pure *sec*-butyl chloride, bromide, and iodide were taken to be 37, 34.2, and 33.5, respectively, ref 6. [c] No attempt was made to determine optimal conditions. [d] Based upon values predicted by the BR–MR method, ref 7. [e] With a few per cent added naphthalene.

$$(C_6H_5)_3M^- + (S)\text{-}(+)\text{-}sec\text{-BuBr} \longrightarrow (R)\text{-}(-)\text{-}sec\text{-BuM}(C_6H_5)_3$$
$$M = \text{Si, Ge, Sn, or Pb}$$

This reaction has all the features of an S_N2 process which apparently always occurs with inversion of configuration. However, the assignment of stereochemistry as inversion of configuration is made with confidence utilizing the correlations of Brewster[6] and Davis and Jensen.[7] For *sec*-butyl compounds, all derivatives (except the deuterio compounds) which are dextrorotatory have the *S* configuration. Other examples of the reactions of organometallic anions with alkyl ha-

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(1) Presented at the Twelfth Conference on Reaction Mechanisms, Brandeis University, June 19–21, 1968.

(2) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, p 96.

(3) K. Sisido, S. Kozima, and K. Takizawa, *Tetrahedron Lett.*, 33 (1967).

(4) H. M. Walborsky and F. J. Impastato, *J. Amer. Chem. Soc.*, **81**, 5835 (1959).

(5) C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, and E. J. Soloski, *J. Org. Chem.*, 27, 619 (1962); H. Gilman, O. L. Maris, and S. Y. Sim, *ibid.*, 27, 4232 (1962).

(6) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

(7) D. D. Davis and F. R. Jensen, *J. Org. Chem.*, **35**, 3410 (1970).