lished g values for semiquinone anions with no halogen substitution fall in the narrow range of 2.0044 ± 0.0004.[2b,9] The values for IV and V (see Table I) occur within this range; however, the value for VI is significantly lower, closely approaching the range 2.0026 ± 0.0001 reported[2b,8] for hydrocarbon radical anions. The nature and unusually low energy of the molecular orbital containing the odd electron anticipates this result. Furthermore, the quantitative theory of g values developed by Stone[10,11] predicts a value of 2.0028, in excellent agreement with the observed one (see Tables I and II). The abnormal a and g values of VI strongly suggest it is not a normal semiquinone anion but more akin to a hydrocarbon anion radical. Since the energy level in which pyracyloquinone can accommodate an extra electron is very low lying and because of the nature of this orbital, the species formed might better be described as a perturbed hydrocarbon radical anion than the semiquinone anion. Theory and experiment and the excellent correlation between them attest to this conclusion.

The distribution of the odd-electron density in this molecule indicates the presence of the pyracylene aromatic system. We have already noted its instability. Furthermore, III is not formed from II under these conditions nor does V, the semiquinone anion of II, decompose to VI. Since diketopyracene (II) may be considered[12] a tautomer of dihydroxypyracylene (III), we might have anticipated interconversion of II and III or of V and VI. This observation and the relative instability of VI suggest the pyracylene aromatic system does not possess the substantial stability predicted by molecular orbital theory.

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[9] (a) M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958); (b) M. S. Blois, H. W. Brown, J. S. Hyde, and J. E. Maling, *Arch. Sci.* (Geneva), **13**, spectrum no. 243–255 (1960); *Chem. Abstr.*, **57**, 1770*b* (1961).

[10] A. J. Stone, *Mol. Phys.*, **6**, 509 (1962).

[11] $g = g_{\mathrm{el}} + b + \lambda c + \rho_{\mathrm{O}}\gamma_{\mathrm{O}}$ where g is the observed value; $g_{\mathrm{el}} = 2.00232$, the value for a free electron; $b = 0.000247$; λ refers to the energy of the odd-electron orbital in the hydrocarbon to which the semiquinone is related (for pyracylene $\lambda = 0.000$); $c = -0.000193$; $\gamma_{\mathrm{O}} = 0.00550$; ρ_{O} is the spin density on oxygen with b, c, and γ_{O} experimental constants as determined by Stone.

[12] The tautomerism required here cannot be considered the normal enol–keto type since enolization requires disruption of one of the benzene rings. This question will be more fully considered in a future communication.

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Substitution Reactions of Sulfitopentaamminecobalt(III) and Its Derivatives. Evidence for a Limiting SN1 Mechanism

Sir:

One of the central themes of recent studies on the mechanisms of substitution reactions of octahedral cobalt(III) ammine complexes has been the question of whether substitution proceeds *via* an SN1 or SN2 mechanism. Arguments in favor of a limiting SN1 mechanism involving a pentacoordinated cobalt(III) intermediate have been advanced for such reactions, but the evidence appears to be inconclusive and the issue has remained a lively and controversial one.[1] We now wish to present definitive kinetic evidence that certain substitution reactions of $\mathrm{Co(NH_3)_5SO_3^+}$ and its derivatives do proceed by limiting SN1 mechanisms involving the intermediate $\mathrm{Co(NH_3)_4SO_3^+}$.[2] Our evidence is essentially similar to that advanced by Haim and Wilmarth[3] for a limiting SN1 mechanism, involving the pentacoordinated intermediate $\mathrm{Co(CN)_5^{2-}}$, in the substitution of water in $\mathrm{Co(CN)_5OH_2^{2-}}$ by various nucleophiles.

Our investigations relate to the series of substitution reactions (where $\mathrm{A = NH_3}$)

$$\mathrm{Co^{III}A_4SO_3(X) + Y \longrightarrow Co^{III}A_4SO_3(Y) + X} \qquad (1)$$

$\mathrm{X = NH_3}$; $\mathrm{Y = {}^{15}NH_3, OH^-, CN^-, NO_2^-}$, or $\mathrm{SCN^-}$

$\mathrm{X = OH^-}$; $\mathrm{Y = NH_3}$ or $\mathrm{CN^-}$

$\mathrm{X = NO_2^-}$; $\mathrm{Y = NH_3}$ or $\mathrm{OH^-}$

$\mathrm{X = SCN^-}$; $\mathrm{Y = NH_3}$

The occurrence of these reactions apparently reflects the marked *trans*-labilizing influence on the S-bonded sulfito ligand.[4–6] Confirmation of this is provided by our observation that under the conditions of these experiments only one (1.1 ± 0.1) of the five ammonia ligands in $\mathrm{CoA_5SO_3^+}$ exchanges with excess $\mathrm{^{15}NH_3}$ (reaction 2). The configurations of the other disubstituted complexes are not known with certainty but are presumably also *trans*.

$$\mathrm{Co(NH_3)_5SO_3^+ + {}^{15}NH_3 \longrightarrow Co(NH_3)_4({}^{15}NH_3)SO_3^+ + NH_3} \qquad (2)$$

The kinetics of the above reactions (apart from reaction 2 whose kinetics were not studied) were examined at 25° in solutions of ionic strength 0.46 (maintained with $\mathrm{NaClO_4}$). The reactions were followed spectrophotometrically, using a stopped-flow apparatus in the cases where the rates were too fast for conventional measurement.

All of the reactions examined exhibited kinetic behavior consistent with the general rate law

$$\frac{-\mathrm{d[CoA_4SO_3(X)]}}{\mathrm{d}t} = \frac{k_1^{\mathrm{X}}k_2^{\mathrm{Y}}\mathrm{[CoA_4SO_3(X)][Y]}}{k_2^{\mathrm{X}}\mathrm{[X]} + k_2^{\mathrm{Y}}\mathrm{[Y]}} \qquad (3)$$

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[1] See, for example, A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964); C. H. Langford, *ibid.*, **4**, 265 (1965).

[2] The designation SN1 as used here conforms to the widely accepted definition, namely that of a substitution mechanism in which a unimolecular dissociation step generates an intermediate which is sufficiently long-lived to exhibit a selective reactivity pattern toward different nucleophiles, which is independent of the leaving group. While we believe that the $\mathrm{CoA_4SO_3^+}$ intermediate in the present case is pentacoordinated, the evidence does not preclude the possibility of rearrangement to a configuration in which $\mathrm{SO_3^{2-}}$ acts as a bidentate ligand.

[3] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962); A. Haim, R. J. Grassi, and W. K. Wilmarth in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31; R. Barca, J. Ellis, M. Tsao, and W. K. Wilmarth, presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, Paper O-83.

[4] J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

[5] A. V. Babaeva and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, **7**, 404 (1962).

[6] W. K. Wilmarth (private communication) and his co-workers have observed what is apparently an analogous labilizing influence of the sulfito ligand in the complex $\mathrm{Co(CN)_4(SO_3)_2^{5-}}$, which undergoes ready aquation to $\mathrm{Co(CN)_4(H_2O)SO_3^{3-}}$.

derived for the mechanism

$$\mathrm{CoA_4SO_3(X)} \underset{k_2^{\mathrm{X}}}{\overset{k_1^{\mathrm{X}}}{\rightleftharpoons}} \mathrm{CoA_4SO_3^+ + X} \tag{4}$$

$$\mathrm{CoA_4SO_3^+ + Y} \xrightarrow{k_2^{\mathrm{Y}}} \mathrm{CoA_4SO_3(Y)} \tag{5}$$

The following reactions exhibited the full rate law described by eq 3 when the concentrations were varied from 0.025 to 0.05 M $\mathrm{SCN^-}$ and 0.08 to 0.32 M $\mathrm{NH_3}$ in the case of reaction 6, and from 9×10^{-3} to 1.9×10^{-2} M $\mathrm{NO_2^-}$ and 0.15 to 0.45 M $\mathrm{NH_3}$ in the case of reaction 7.

$$\mathrm{CoA_4SO_3(SCN) + A \longrightarrow CoA_5SO_3^+ + SCN^-} \tag{6}$$

$$\mathrm{CoA_4SO_3(NO_2) + A \longrightarrow CoA_5SO_3^+ + NO_2^-} \tag{7}$$

The kinetic data yielded the values $k_1^{\mathrm{SCN^-}} = 1.75$ sec^{-1}, $k_2^{\mathrm{SCN^-}}/k_2^{\mathrm{A}} = 30$, $k_1^{\mathrm{NO_2^-}} = 0.46$ sec^{-1}, and $k_2^{\mathrm{NO_2^-}}/k_2^{\mathrm{A}} = 70$.

Reaction 8, examined over the concentration ranges 0.03 to 0.7 M $\mathrm{NH_3}$ and 1.3×10^{-5} to 2.0×10^{-4} M $\mathrm{OH^-}$, exhibited a rate law which at the higher $\mathrm{OH^-}$ concentrations approached the limiting form described by eq 3 and yielded the values $k_1^{\mathrm{OH^-}} = 7$ sec^{-1} and $k_2^{\mathrm{OH^-}}/k_2^{\mathrm{A}} = 8 \times 10^3$. At lower $\mathrm{OH^-}$ concentrations an additional contribution from a path involving $\mathrm{CoA_4(OH_2)SO_3^+}$ was indicated.

$$\mathrm{CoA_4SO_3(OH) + A \longrightarrow CoA_5SO_3^+ + OH^-} \tag{8}$$

In the case of the other reactions only a limiting form of the rate law described in eq 3 was observed owing to domination of one or other of the terms in the denominator. Thus, the series of reactions

$$\mathrm{CoA_5SO_3^+ + Y^- \longrightarrow CoA_4SO_3(Y) + A} \tag{9}$$

(where $\mathrm{Y^-} = \mathrm{OH^-}$, $\mathrm{CN^-}$, $\mathrm{NO_2^-}$, and $\mathrm{SCN^-}$), when the concentrations of $\mathrm{Y^-}$ and A were such that the reactions proceeded in the direction indicated (typically in the ranges 0.01 to 0.1 M A and 0.01 to 0.4 M $\mathrm{Y^-}$), all exhibited the same limiting first-order rate law $-\mathrm{d} \ln [\mathrm{CoA_5SO_3^+}]/\mathrm{d}t = k_1^{\mathrm{A}} = (1.2 \pm 0.1) \times 10^{-2}$ sec^{-1} (independent of $\mathrm{Y^-}$) in agreement with eq 3, when $k_2^{\mathrm{Y}}[\mathrm{Y}] >> k_2^{\mathrm{X}}[\mathrm{X}]$. The equilibrium constants for reactions 6 and 8, computed from the above kinetic data, were in excellent agreement with the spectrophotometrically measured values of 4.9 and 7×10^{-2}, respectively.

Reaction 10, examined over the concentration range 0.05 M A, 0.1 to 0.4 M $\mathrm{OH^-}$, and 5.0×10^{-3} to 4.0×10^{-2} M $\mathrm{CN^-}$, exhibited the rate law $-\mathrm{d}[\mathrm{CoA_4SO_3(OH)}]/\mathrm{d}t = k'[\mathrm{CoA_4SO_3(OH)}][\mathrm{CN^-}]/[\mathrm{OH^-}]$, consistent with the limiting form of eq 3 when $k_2^{\mathrm{OH^-}}[\mathrm{OH^-}] >> k_2^{\mathrm{CN^-}}[\mathrm{CN^-}]$ and yielding $k' = k_1^{\mathrm{OH^-}} k_2^{\mathrm{CN^-}}/k_2^{\mathrm{OH^-}} = 3.8 \times 10^{-2}$ sec^{-1}.

$$\mathrm{CoA_4SO_3(OH) + CN^- \longrightarrow CoA_4SO_3(CN) + OH^-} \tag{10}$$

We conclude that all of these reactions proceed through limiting SN1 mechanisms (eq 4 and 5) involving the common intermediate $\mathrm{CoA_4SO_3^+}$. From the kinetic data the following values have been obtained for the dissociation constants (k_1^{X}) of the various complexes $\mathrm{CoA_4SO_3(X)}$ and the relative reactivities (k_2^{X}) of various nucleophiles (X) toward $\mathrm{CoA_4SO_3^+}$.

X	$\mathrm{NH_3}$	$\mathrm{NO_2^-}$	$\mathrm{SCN^-}$	$\mathrm{CN^-}$	$\mathrm{OH^-}$
k_1^{X}, sec^{-1}	1.2×10^{-2}	0.46	1.75	..	7
$k_2^{\mathrm{X}}/k_2^{\mathrm{A}}$	1	70	30	43	8×10^3

For comparison, the corresponding values obtained by Wilmarth, *et al.*,[3] for the relative reactivities of some of the same nucleophiles toward $\mathrm{Co(CN)_5^{2-}}$ are $k_2^{\mathrm{SCN^-}}/k_2^{\mathrm{A}} = 2.3$ and $k_2^{\mathrm{OH^-}}/k_2^{\mathrm{A}} = 1.1 \times 10^4$.

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A Unique Reversal of Stereospecificity in the Addition of Phenyllithium *vs.* Phenylmagnesium Bromide to 1,2-Dicyclohexylethanedione-C^{14}

Sir:

As part of a continuing study by isotope dilution techniques of the quantitative stereochemistry of the addition of organometallic reagents to α-diketones and ketols,[1,2] both phenyllithium and phenylmagnesium bromide, respectively, were added in excess to carbon-14 labeled 1,2-dicyclohexylethanedione. Phenyllithium gave exclusively the *dl*-racemic glycol, 1,2-diphenyl-1,2-dicyclohexylethanediol (57.6% yield, ether solution, 11-hr reaction time); less than 0.25% of the *meso* form, well within the limits of the technique, was found. Phenylmagnesium bromide produced solely the *meso* glycol (14.8% yield, ether solution, 5 days reaction time); similarly, less than 0.25% of the racemate form was observed. Substitution of phenylmagnesium iodide gave rise to less than 0.5% of glycol in 8 days reaction time. The results of the quantitative studies were reflected in macro runs, utilized in the case of the phenyllithium to prepare dilution materials. The *meso* glycol was prepared, in turn, by careful seeding of the crude glycolic product isolated from the zinc–sulfuric acid reduction in aqueous ethanol of phenyl cyclohexyl ketone.[3] Assignment of diastereoisomeric identity rested on infrared[4] and nmr[5] spectroscopic data. The synthesis of the labeled diketone has been described.[2]

A simple reversal of predominant diastereoisomer formed has been reported previously for these reagents on two occasions;[1,6] there do not appear to be any previous reports of a stereospecific reversal of behavior. The present extreme case further emphasizes the puzzle.

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(1) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960).

(2) J. H. Stocker, *J. Org. Chem.*, **29**, 3593 (1964).

(3) These glycols have been reported twice in the literature. Prepared similarly to the metal–acid procedure above by O. Neunhoeffer and F. Nerdel [*Ann.*, **526**, 47 (1936)], they were separated by fractional crystallization and reported to melt at 160 and 198°, respectively. They were subsequently prepared by Y. Yukawa and T. Hanabusa [*J. Chem. Soc. Japan, Pure Chem. Section*, **82**, 1724 (1961)], similarly separated, and reported to melt at 167–171 and 194–197°, respectively. The glycols employed as dilution materials in the present study showed melting points of 179–180 and 208–209°, respectively. They were analytically pure and both rearranged under the influence of strong acid by phenyl migration to the same ketone.

(4) See, *e.g.*, W. A. Mosher and N. D. Heindel, *J. Org. Chem.*, **28**, 2154 (1963), and references cited therein.

(5) The hydroxylic proton resonance of the *meso*-glycol appears at higher field strength than that of the racemic isomer. This appears to be a general phenomenon. (Private communication from B. M. Benjamin, Oak Ridge National Laboratory.) See also J. Wieman, G. Dana, Sa-Le-Thi-Thuan, M. Brami, and M. Delépine, *Compt. Rend.*, **258**, 3724 (1964).

(6) J. Yoshimura, Y. Ohgo, and T. Sato, *J. Am. Chem. Soc.*, **86**, 3958 (1964). These authors were investigating substitution rather than addition reactions and the situations are probably not analogous.