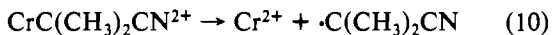


formation process is reversed and the material lost prior to isolation (eq 10). This proposal requires no special reactivity



for complexes formed from α -cyano radicals and is completely consistent with the long lifetime of the relatively unhindered $\text{CrCH}_2\text{CN}^{2+}$ and with the chemistry of the closely related α -hydroxyalkyl analogues. It may be possible to stabilize $\text{CrC}(\text{CH}_3)_2\text{CN}^{2+}$ against homolysis by addition of excess Cr^{2+} , just as $\text{CrC}(\text{CH}_3)_2\text{OH}^{2+}$ can be stabilized, but this was not investigated.

The complexes investigated were not subject to detectable homolysis as evidenced by lack of ready reaction with reagents such as Cu^{2+} , Fe^{3+} , and $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ which would scavenge a product from a reaction analogous to eq 10. This lack of reactivity is not surprising for these complexes again because the α -carbon atom is relatively unsubstituted. And the unhindered $\text{CrCH}_2\text{CN}^{2+}$, like $\text{CrCH}_2\text{OH}^{2+}$, would not tend to undergo ready homolysis.

Reactions of Hg^{2+} with alkylchromium(III) complexes have been studied in some detail¹⁴ and are recognized as electrophilic processes involving direct attack of Hg^{2+} at the α -carbon. The present data are in keeping with this picture in several respects: (1) an electronegative substituent on the carbon atom bound to chromium (as in $\text{CrCH}_2\text{X}^{2+}$) greatly lowers the rate of reaction; compare, for example, $\text{CrCH}_2\text{CH}_3^{2+}$ ($k_{\text{Hg}} = 1.40 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)¹⁴ to $\text{CrCH}_2\text{Cl}^{2+}$ ($5.90 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$),¹⁴ $\text{CrCH}_2\text{OH}^{2+}$ ($2.3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$),¹³ and the present $\text{CrCH}_2\text{CN}^{2+}$ ($9.84 \text{ M}^{-1} \text{ s}^{-1}$); (2) substitution β to chromium has minimal effect. For example the three complexes studied here all show nearly the same reactivity (within a factor of 9), just as alkylcobaloximes do¹⁵ for the similarly substituted analogues with ethyl, *n*-propyl, and isobutyl groups. Alternatively one can compare the relative reactivities of

$\text{CrCH}_2\text{CH}_3^{2+}$ and $\text{CrCH}_2\text{CH}_2\text{CH}_3^{2+}$ (relative rate, 4.0:1.0) with $\text{CrCH}_2\text{CH}_2\text{CN}^{2+}$ and $\text{CrCH}_2\text{CH}(\text{CH}_3)\text{CN}^{2+}$ (3.2:1.0). It should be noted, in view of the well-recognized sensitivity of rates of such reactions to α substituents and their insensitivity to β substituents, that the kinetic data provide confirming evidence of the structure assigned to the complexes; complexes derived from the products of eq 3a and 4a would be expected to react very much slower.

Experimental Section

The chemicals were purchased as reagent-grade materials or prepared as described previously.^{4,8,12} The reactions to prepare the new cyanoalkyls were conducted by dripping a deaerated solution of hydrogen peroxide in dilute perchloric acid into a well-stirred aqueous solution of $\text{Cr}(\text{ClO}_4)_2$ containing some 3-8% by volume of the desired nitrile until H_2O_2 was in ca. 10% excess. The complexes were absorbed onto a column of Dowex 50W-X8 which was then rinsed free of nitrile and excess peroxide with use of 0.02 M perchloric acid, followed by elution of the dipositive organochromium cation with 0.7-0.8 M acid, leaving $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ on the resin column. The complexes were isolated and stored under nitrogen because they decomposed notably faster when exposed to air. The absorption spectra are given in Table I. The molar absorptivities were based on spectrophotometric analysis of the complexes as chromate ions after heating in alkaline peroxide. Yields of the (cyanoalkyl)chromium(III) ions were not determined, but especially low conversion to $\text{CrCH}_2\text{CN}^{2+}$ was noted. The β -cyanoalkyl complexes were also formed in considerably less than the theoretical quantity, consistent with the suggested homolytic decomposition of any α -cyanoalkyl complex formed.

Bromination reactions were conducted by slowly adding aqueous bromine in slightly less than the required amount and then extracting products into methylene chloride. Procedures for the kinetic experiments were described previously.¹⁴

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021, under Contract W-7405-ENG-82.

Registry No. $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CN}^{2+}$, 76068-68-3; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH}_2\text{CN}^{2+}$, 76068-69-4; $(\text{H}_2\text{O})_5\text{CrCH}_2\text{CH}(\text{CH}_3)\text{CN}^{2+}$, 76068-70-7; CH_3CN , 75-05-8; $\text{CH}_3\text{CH}_2\text{CN}$, 107-12-0; $(\text{CH}_3)_2\text{CHCN}$, 78-82-0; Hg^{2+} , 7439-97-6.

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Contribution from the Institute for Chemical Research, Kyoto University, Uji 611, Japan, and the Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuho-ku, Nagoya 467, Japan

Kinetics and Mechanism of Iodination of Para-Substituted Benzylbis(dimethylglyoximate)(pyridine)cobalt(III). High Reactivity of the Base-Off Form

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A kinetic study of the iodination of $p\text{-XC}_6\text{H}_4\text{CH}_2\text{Co}(\text{DH})_2(\text{py})$ (X = methoxy, methyl, H, chloro, nitro; DH = monoanion of dimethylglyoxime; py = pyridine) revealed the rate-determining dissociation of pyridine and subsequent rapid reaction of the base-free form with iodine. The high reactivity of the base-free form is discussed in relation to inner-sphere electron transfer. The rates of dissociation of pyridine showed a Hammett-like linear free-energy relationship with a ρ^+ of -1.48.

The mechanism of cleavage of the carbon-cobalt bond is a subject of considerable interest because of the importance in vitamin B_{12} chemistry, and evidence as to the formation and participation of radical species in the cleavage of the carbon-cobalt bond has accumulated in both chemical and biological fields. Reversible generation of organic free radicals and B_{12r} was detected during the coenzyme B_{12} -dependent

reactions with dioldehydrase³ and ethanolamine ammonia-lyase,⁴ an alkyl-cobalt bond dissociates on photolysis into an organic free radical and cobalt(II),⁵ and free-radical substi-

(1) Kyoto University.

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Table I. Product Analyses of Iodination of Para-Substituted Benzylbis(dimethylglyoximate)(pyridine)cobalt(III)^a

| substituent X | product yield, % | |
|-------------------|--|---------------------------|
| | XC ₆ H ₄ CH ₂ I | ICo(DH) ₂ (py) |
| CH ₃ O | 72 | 98 |
| H | 99 | 90 |
| NO ₂ | 100 | 94 |

^a In benzene at 40 °C.

tution takes place for benzyl-, allyl-, and allenylcobalt(III) complexes.⁶⁻⁸ Even some of the apparent electrophilic substitution reactions of organometallic complexes proceed via successive reactions with an initial electron transfer from a metal complex to electrophiles, generating an organometallic cation radical, the reaction of which with external nucleophiles or free radicals gives final products.⁹

Halogenation of organobis(dimethylglyoximate)cobalt(III) has been suggested as taking place by the successive reactions via Co(IV)¹⁰ on the basis of the inversion of the stereochemistry of organic products¹¹ and the product distribution of the reaction with iodine monochloride.^{12,13} Although the reaction has long been known, a kinetic study has not been reported.

As for the structure of cobalt(III) complexes, a six-coordinate octahedral configuration is the most abundant and a pentacoordinate base-free complex is found less frequently as a stable form. The latter is, however, postulated as an intermediate in the ligand-exchange reaction and has been the subject of discussion.¹⁴ The importance of the five-coordinate complex is also noted for iron complexes. Molecular oxygen reacts easily with five-coordinate iron(II) porphyrins to give μ -oxo iron(III) dimers.¹⁵ A six-coordinate base-on form is unreactive. Thus base-off five-coordinate complexes are expected to contribute as reactive intermediates in reactions of cobalt complexes other than ligand-exchange processes such as oxidation-reduction, but little is known so far. The contribution of a five-coordinate base-free form in the reaction of molecular oxygen with alkylbis(dimethylglyoximate)(pyridine)cobalt(III) was reported,¹⁶ but the result was criticized.¹⁷

A kinetic study of iodination of para-substituted benzylbis(dimethylglyoximate)(pyridine)cobalt(III) revealed marked reactivity of the five-coordinate base-free complex toward iodine, which is the subject of the present article.

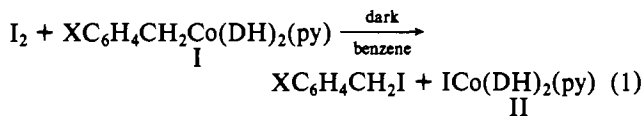
Table II. Kinetic Results of Iodination of Substituted Benzylcobaloximes^a

| substrate | 10 ⁵ × [substrate], M | 10 ³ × [I ₂], M | 10 ⁴ × [HgI ₂], M | 10 ⁴ × k _{obsd} , s ⁻¹ | |
|---|----------------------------------|--|--|---|------|
| Ia (X = H) | 1.00 | 4.00 | 0 | 3.63 | |
| | 1.00 | 2.70 | 0 | 3.20 | |
| | 5.00 | 1.50 | 0 | 3.27 | |
| | 7.00 | 1.50 | 0 | 3.52 | |
| | 11.5 | 1.50 | 0 | 2.91 | |
| | 11.5 | 0.50 | 0 | 3.31 | |
| | 10.5 | 0.14 | 0 | 2.90 | |
| | 11.1 | 0.05 | 0 | 2.89 | |
| | 5.00 | 1.50 | 5.00 | 3.12 | |
| | 5.00 | 1.50 | 3.33 | 3.42 | |
| | 5.00 | 1.50 | 1.67 | 2.46 | |
| | 5.00 | 1.50 | 0.05 | 4.07 | |
| | Ib (X = CH ₃) | 11.5 | 1.50 | 0 | 6.69 |
| | | 5.00 | 1.50 | 0 | 5.86 |
| | | 5.00 | 1.50 | 0 | 7.93 |
| 7.00 | | 0.50 | 0 | 5.47 | |
| 5.00 | | 1.50 | 3.33 | 6.47 | |
| 5.00 | | 1.50 | 1.67 | 9.84 | |
| 5.00 | | 1.50 | 0.83 | 7.19 | |
| 5.00 | | 1.50 | 0.16 | 8.17 | |
| 5.00 | | 1.50 | 0.05 | 9.02 | |
| Ic (X = CH ₃ O) | | 5.00 | 1.50 | 0 | 60.1 |
| | 1.50 | 0.46 | 0 | 59.5 | |
| | 1.50 | 0.23 | 0 | 59.6 | |
| | 5.00 | 1.50 | 5.00 | 74.2 | |
| | 5.00 | 1.50 | 3.33 | 70.0 | |
| | 5.00 | 1.50 | 1.67 | 52.1 | |
| | 5.00 | 1.50 | 0.83 | 64.1 | |
| | 5.00 | 1.50 | 0.31 | 34.8 | |
| | 5.00 | 1.50 | 0.05 | 74.8 | |
| | Id (X = Cl) | 5.00 | 3.00 | 0 | 3.00 |
| 5.00 | | 1.00 | 0 | 1.70 | |
| 5.00 | | 0.10 | 0 | 2.70 | |
| Ie (X = NO ₂) | 1.10 | 1.50 | 0 | 0.417 | |
| | 1.10 | 0.14 | 0 | 0.432 | |
| If (X = CH ₃ O, py = <i>p</i> -methylpyridine) | 5.00 | 2.50 | 0 | 52.5 | |
| | 5.00 | 1.50 | 0 | 46.9 | |
| | 5.00 | 1.50 | 0 | 52.3 | |
| | 5.00 | 1.50 | 0 | 49.2 | |
| | 5.00 | 1.50 | 0 | 60.5 | |
| | 5.00 | 1.50 | 0 | 60.5 | |
| | 5.00 | 1.10 | 0 | 63.1 | |
| | 5.00 | 1.10 | 0 | 63.1 | |

^a In benzene at 40 °C.

Results and Discussion

Stoichiometry was determined for benzyl, *p*-methoxybenzyl, and *p*-nitrobenzyl complexes by spectrophotometric titration. A distinct break point was found at the ratio of concentrations, [I₂]/[Co(III)], of 1.0 for each reaction, and the spectrum at that ratio was a superposition of spectra of the appropriate concentrations of iodobis(dimethylglyoximate)(pyridine)cobalt(III) and the substituted benzyl iodide. Product analyses listed in Table I show the presence of only two products described above. These results confirm the stoichiometry expressed by eq 1. Yields were nearly quantitative except for

X: a, H; b, CH₃; c, CH₃O; d, Cl; e, NO₂

the *p*-methoxy derivative. The relatively low yield of *p*-methoxybenzyl iodide is due to Friedel-Crafts type condensation of eq 2. A mixture of dimers was separated by column chromatography in a yield of 19%, and presence of higher

$$2CH_3OC_6H_4CH_2I \rightarrow (CH_3OC_6H_4CH_2)_2Co(DH)_2(py) + HI \quad (2)$$

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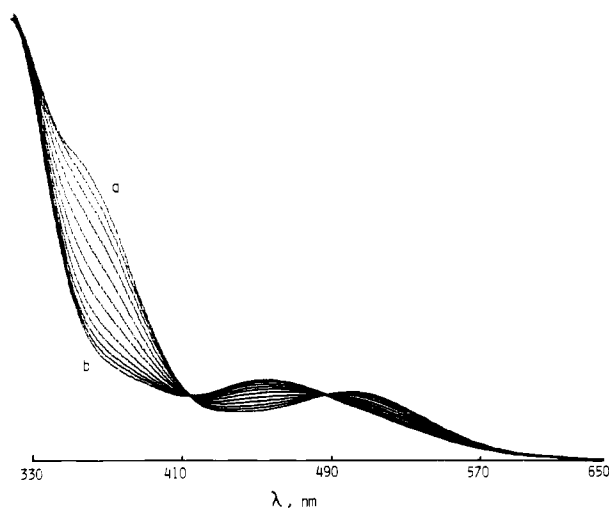


Figure 1. Spectra of the iodination of Ia: a, initial; b, final.

condensation products up to the tetramer was detected by mass spectroscopy. No dimethylglyoxime O-benzyl ether or corresponding diarylethane was present in the products of the three complexes examined. Thus iodination of complex I in benzene is a clean reaction producing substituted benzyl iodide and II as the sole products in marked contrast to the complicated feature of bromination.¹⁸ The simple mechanism of iodination would arise partly from the inert character of iodine in the electrophilic substitution of the aromatic ring¹⁹ and the high electron affinity of iodine.²⁰ The slight difference in the products compared with those in acetic acid^{18a} might be due to the low polarity of benzene.

Kinetics were measured spectrophotometrically. The time-dependent change of spectra showed distinct isosbestic points at 417 and 483 nm for reaction of Ia as shown in Figure 1. The results of stoichiometry and the presence of isosbestic points indicate that the observed spectral change corresponds to the decrease in concentration of Co(III) complexes as shown in eq 3. When the concentration of iodine is in excess com-

$$\frac{d[(A_t - A_\infty)/(A_0 - A_\infty)]}{dt} = \frac{d[[I]_t/[I]_0]}{dt} \quad (3)$$

pared with that of complex I, the rate of disappearance of complex I followed a good pseudo-first-order kinetics with a correlation coefficient of more than 0.999 over at least 90% of each reaction (eq 4). The results are listed in Table II.

$$-\frac{d[I]}{dt} = k_{\text{obsd}}[I] \quad (4)$$

As can be seen from Table II, the rate constants were independent of the concentration of iodine.

With an excess of Co(III) the rate was apparently constant over 90% of completion. The rate constant under a condition of Ia (4.62×10^{-4} M) and I₂ (9.24×10^{-5} M) was 3.18×10^{-4} s⁻¹, which is identical with that found under the conditions of iodine in excess ($(3.23 \pm 0.42) \times 10^{-4}$ s⁻¹) within the limit of experimental error.

The agreement of rate constants over a wide range of concentrations indicates that the same mechanism operates throughout the ranges of concentration. Lack of dependence of the rate on iodine concentration strongly suggests that the rate-limiting step is unimolecular dissociation of complex I.

Table III. Dependence of Rate of Iodination of Ic on Pyridine Concentration^a

| 10 ⁴ [py], M | 10 ³ k _{obsd} , s ⁻¹ | 10 ⁻² k _{obsd} ⁻¹ , s |
|-------------------------|---|--|
| 0 | 6.01 | 1.66 |
| 32.2 | 4.95 | 2.02 |
| 62.5 | 3.54 | 2.84 |
| 90.9 | 3.28 | 3.05 |
| 117.6 | 2.95 | 3.39 |
| 142.9 | 2.63 | 3.80 |

^a [I₂] = 1.5×10^{-3} M and [complex Ic] = 5.0×10^{-5} M in benzene at 40.0 ± 0.1 °C measured at 370 nm.

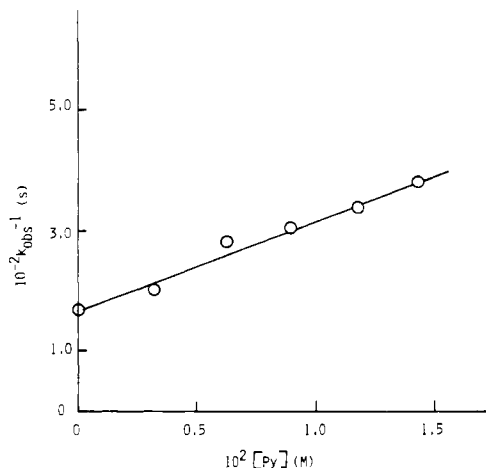


Figure 2. Dependence of the rate of iodination on pyridine concentration: Ic, 5.00×10^{-5} M; I₂, 1.5×10^{-3} M.

Although there are some reports on the thermal homolytic dissociation of the alkyl-cobalt bond,^{8,21} complex Ia does not react with radical scavengers such as galvinoxyl and nitrosodurene under the present reaction conditions. A C₆D₆ solution of complex Ia showed no change in the ¹H NMR spectra in the presence of molecular oxygen at 40 °C in 20 h. As the concentration of oxygen saturated in benzene is 1.6×10^{-2} M at 40 °C,²² which is about 7 times as large as that of iodine generally used in the present experiments, there is thus sufficient evidence against rate-determining homolytic unimolecular dissociation of the benzyl-cobalt bond. A free-radical chain reaction has been reported to be initiated with a cobalt(II) impurity by Johnson and others for the reaction with bromotrchloromethane,⁶⁻⁸ but BrCCl₃ fails to react with complex Ia under the present reaction conditions.

Unimolecular heterolytic cleavage of the carbon-cobalt bond is less plausible in a nonpolar solvent such as benzene. Another possible mechanism is electrophilic substitution of complex I with iodine.⁹ The addition of bis(pyridine)iodonium perchlorate did not show remarkable acceleration. Other electrophiles such as mercury(II) chloride, mercury(II) acetate, and nitrosyl chloride were inactive or far less reactive than iodine.²³ Presence of mercury(II) iodide in the iodination reaction had no influence on the rate of reaction (Table II). As iodine is a less reactive electrophile than mercury(II) ion,²⁵

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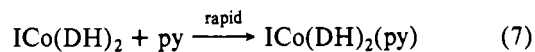
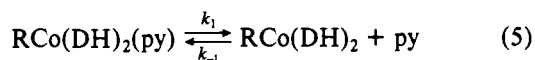
Table IV. Rate Constants of Dissociation of Pyridines from Para-Substituted Benzylbis(dimethylglyoximate)(pyridine)cobalt(III)^a

| pyridine | substituent | 10 ⁴ k ₁ , s ⁻¹ |
|------------------|------------------|--|
| pyridine | NO ₂ | 0.425 ± 0.011 |
| pyridine | Cl | 2.47 ± 0.68 |
| pyridine | H | 3.23 ± 0.42 |
| pyridine | CH ₃ | 7.43 ± 1.44 |
| pyridine | OCH ₃ | 61.2 ± 13.2 |
| p-methylpyridine | OCH ₃ | 54.1 ± 6.4 |

^a In benzene at 40 °C.

present results eliminate the possibility of the mechanism of electrophilic substitution.

The rate was dependent on the concentration of pyridine as is shown in Table III. Reciprocal plots of the observed rate constant against pyridine concentration are shown in Figure 2. Under the conditions of constant iodine concentration, a linear relationship was observed. This dependency is consistent with the mechanism of eq 5–7. The mechanism

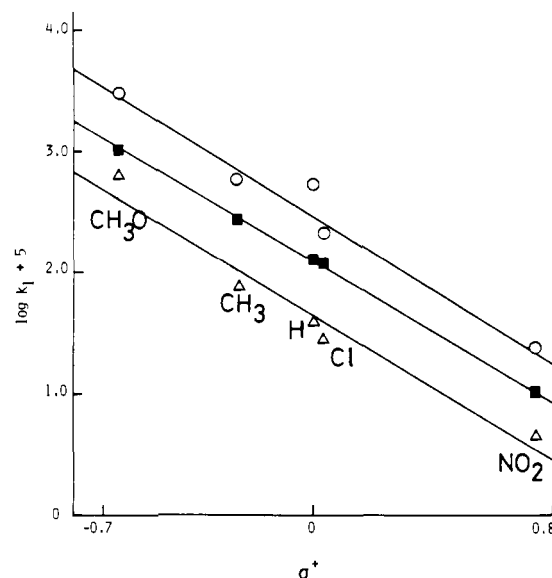


leads to the rate expression of eq 8. The rate constant k_1 and

$$-\frac{d[\text{I}]}{dt} = \frac{k_1 k_2 [\text{I}][\text{I}_2]}{k_{-1}[\text{py}] + k_2[\text{I}_2]} = \frac{k_1[\text{I}]}{1 + k_{-1}[\text{py}]/k_2[\text{I}_2]} \quad (8)$$

the ratio of k_{-1}/k_2 of complex Ic is estimated from the intercept and the slope of Figure 2 as follows: $k_1 = (6.00 \pm 0.33) \times 10^{-3} \text{ s}^{-1}$ and $k_{-1}/k_2 = (1.36 \pm 0.09) \times 10^{-1}$. With no extra addition of pyridine, the concentration of iodine was 30 times as large as that of complex I, to which the maximum concentration of pyridine is limited. In addition, the concentration of free pyridine in equilibrium would be very low because of the high reactivity of five-coordinated complexes in the ligand-exchange reactions. The ratio of k_{-1}/k_2 will vary with the benzyl substituent, but the small value of the pyridine to iodine concentration ratio makes the second term in the denominator small enough to be negligible compared with 1.0. Therefore the observed pseudo-first-order rate constant corresponds to the rate constant of dissociation, k_1 . Slow formation of strongly colored pyridinium ion made it difficult to determine k_{-1}/k_2 for complexes other than complex Ic.

The rate constants of dissociation of pyridine are listed in Table IV. Electron-releasing para-substituents of the benzyl group increased the rate of reaction, and introduction of the 4-methyl group in the pyridine ring made the rate less although the effect is not large. A good Hammett-type relationship was present between the rate constants and σ^+ ²⁶ with a ρ^+ value of -1.48 at 40 °C as shown in Figure 3. The effect is larger than that for the electrophilic substitution reaction of the same substrate with mercury(II) ion ($\rho = -1.18$)²⁴ and bromination or iodination of para-substituted benzylpentaquochromium(III).²⁷ The Hammett-type relationship pertaining to the trans effect has been reported only for the dissociation of pyridine from alkylbis(dimethylglyoximate)(pyridine)cobalt(III) in water. The ρ value is -4.13 against Taft's σ^* .²⁸ The effect of the benzyl substituent is smaller because of the more distant position of substitution, but the effect is large considering that the reaction center, the cobalt-pyridine bond, is isolated from

**Figure 3.** Linear free-energy relationship for dissociation of pyridine from Ia-e: Δ , 40 °C; \blacksquare , 50 °C; \circ , 60 °C.**Table V.** Kinetic Parameters of Dissociation of Pyridine from Para-Substituted Benzylbis(dimethylglyoximate)(pyridine)cobalt(III)^a

| substrate | ΔH^\ddagger , kcal mol ⁻¹ | ΔS^\ddagger , cal mol ⁻¹ deg ⁻¹ |
|-----------|--|---|
| Ic | 20.0 ± 0.6 | -5.6 ± 1.0 |
| Ib | 20.4 ± 0.1 | -7.0 ± 0.2 |
| Ia | 20.8 ± 0.6 | -7.7 ± 1.0 |
| Id | 21.0 ± 0.7 | -8.0 ± 1.3 |
| Ie | 22.2 ± 2.1 | -8.4 ± 4.8 |

^a Calculation was carried out for the values of each substituted complex on the lines of Figure 4. Values of ΔH^\ddagger (kcal mol⁻¹) and ΔS^\ddagger (cal mol⁻¹ deg⁻¹) obtained from the original experimental values are respectively as follows: Ic, 15.9 ± 2.7, -18.3 ± 4.8; Ib, 20.6 ± 1.8, -6.8 ± 3.3; Ia, 27.9 ± 0.4, 14.5 ± 7.0; Id, 21.5 ± 4.0, -6.3 ± 5.4; Ie, 18.1 ± 0.1, -23.0 ± 0.2.

the conjugation of the benzene ring by a methylene group. The reaction center of the electrophilic substitution of complex I with mercury(II) ion is the benzylic carbon itself, but the ρ value is a little smaller. Therefore the effect of the substituent on the benzene ring seems to be effectively transmitted to cobalt through the methylene group. As the effect of substituents is not transmitted effectively through σ bonds, the result suggests some extent of π character in the bonding between cobalt and carbon, or there might be a contribution of σ - π conjugation.²⁹ The better correlation with σ^+ rather than σ indicates that the resonance effect of the para substituent extends through the benzylic carbon to the reaction center and thus supports the above assumption.

The larger substituent effect on ligand dissociation compared with the electrophilic substitution by mercury(II) ion might be explained also by the parallel and perpendicular effect of the substituent at the transition state.³⁰ Pyridine dissociates along the reaction coordinate which is almost parallel to the benzene ring, whereas the approach of the Hg(II) ion and departure of the cobalt complex takes place at a perpendicular position to the benzene ring. The substituents on a benzene ring which is perpendicular to the reaction coordinate gives a smaller substituent effect.

The kinetic parameters measured at the temperature range of 40–60 °C are summarized in Table V. The values of ΔH^\ddagger lie within the range of reported values for the base exchange of methylbis(dimethylglyoximate)cobalt(III) complexes by

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NMR methods.^{31,32} Entropy of activation was negative, in contrast to the dissociation of trimethyl phosphite in toluene-*d*₆,³² which has a positive entropy of activation. Negative values of ΔS^\ddagger suggest the increase in solvation at the transition state. Although the rate constants did not significantly change with temperature, there is a distinct trend in the substituent effect. In the order of the increasing effect of substituents, ΔH^\ddagger becomes less in accordance with the higher trans effect. The entropy of activation increases in this order. The tendency is in accordance with a reactant-like transition state in the case of an electron-releasing group and a product-like transition state for the more stable complex of an electron-withdrawing substituent on the benzene ring.

In the mechanism presented above, a purely dissociative mechanism for pyridine dissociation is assumed in eq 5 instead of a dissociative interchange. If the reaction proceeds through a dissociative interchange, the independence of the observed rate constants to the iodine concentration would require the fast and complete coordination of iodine to complex I. ¹H NMR spectra of complexes Ia–e were measured at –50 °C in CDCl₃ to check this point. Addition of iodine showed a slight downfield shift, but the shifts had no systematic trend. The signals did not show any broadening. These observations indicate that the small shift is caused by a change of medium. In addition, the apparent zero-order kinetics with benzylcobalt in excess is inconsistent with the assumption of complete coordination of iodine. The absorption of I₂–benzene at 500 nm did not show any faster change, and the monotonic change of absorbances in the whole wavelength excludes a prior complex formation between iodine and the substrates.

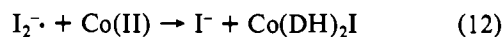
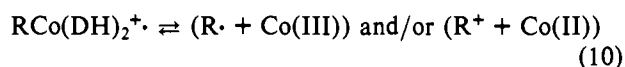
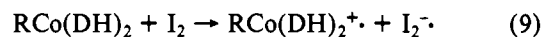
The exclusive reaction of iodine with the base-off form is worthy of note. The high reactivity of the base-off form has been found in the electrochemical reduction of vitamin B_{12a}.³³ The base-off form is reduced 150 times faster than the base-on form.

The preference of the base-on form over the base-off form has been proposed by Kiskis and Jensen for the insertion of dioxygen into the cobalt–carbon bonds of several alkyl(pyridine)cobaloximes on the ground that addition of pyridine has no effect on the rate of thermal reaction.¹⁷ The rationale for the higher reactivity of the base-off form is difficult to draw, but the facility of inner-sphere oxidation of cobalt(II)³⁴ and other bivalent metal complexes³⁵ by iodine suggests that a similar inner-sphere electron-transfer mechanism with iodine as electrophile is operating here in preference to an outer-sphere electron transfer of the six-coordinate base-on form. A close analogy to the present result is found in the reaction of oxygen with heme, which proceeds easily with a five-coordinate form but does not react easily with a six-coordinate form.¹⁵ Electrophilic substitution of methyl B₁₂ and methylcobalamin by mercury(II)³⁶ and tetrachloropalladate(II),³⁷ however, showed the reverse reactivity. In these cases the base-on form is more reactive than the base-off form, in which an electrophile coordinates on the base.

As described earlier, the stereochemistry of halogenation of alkylbis(dimethylglyoximate)cobalt(III) complexes has been shown to proceed with inversion in dichloromethane,¹¹ which is accepted as evidence for successive reactions with initial electron transfer. In contrast, retention of stereochemistry has

been reported for electrophilic substitution of optically active derivatives of alkylpentacarbonylmanganese(I)³⁸ and alkyl-dicyclopentadienylchlorozirconium(IV).³⁹ The stereochemistry of the present system was examined with an optically active (phenylethyl)bis(dimethylglyoximate)(pyridine)cobalt(III) to confirm occurrence of successive reactions. Iodination was carried out in the presence of tetra-*n*-butylammonium chloride because 1-phenylethyl iodide, the product, is too unstable to be isolated for determination of optical purity. If the reaction takes place through the successive reactions, the high concentration of chloride ion would facilitate the nucleophilic substitution of the cation radical to give phenylethyl chloride with inversion of the configuration. Eventually 1-phenylethyl chloride was isolated by a silica-gel column in a yield of 56%. The corresponding iodide was not found in the products, but a substantial amount of styrene was present. Phenylethyl chloride thus isolated showed a 3.0 ± 0.3% excess of inversion product. The stability of the (1-phenylethyl)bis(dimethylglyoximate)cobalt(IV) cation radical is expected to be low because this would dissociate easily in a cage into a resonance-stabilized stable (phenylethyl)carbenium ion or a radical and cobalt(II) or cobalt(III), respectively, to bring about the loss of optical activity. The figure presents sufficient evidence for the successive reactions. The presence of styrene in the product suggests partial dissociation of the cation radical into a free (phenylethyl)carbenium ion and cobalt(II),¹² but corresponding dissociation into an organic free radical and cobalt(III) would be less probable because of the absence of dimerization product.

Therefore, it is proposed that the iodination of base-free complex I proceeds by a mechanism with initial electron transfer as represented by eq 9–12. A possible fate of the cation radical is shown in eq 11.



Thus the high reactivity of the five-coordinate cobalt(III) complex in the oxidation process has been demonstrated. The result tends to confirm the importance of the five-coordinate form in the redox reaction of hemoproteins exemplified by myoglobin and hemoglobin which have five-coordinate iron(II) protected from unfavorable irreversible reaction by globin.¹⁵ A five-coordinate form is also noted for oxygenases, peroxidases, and cytochrome *P*-450.⁴⁰

Experimental Section

Substituted benzylcobalt complexes were sensitive to light, and all experiments were carried out in the dark. Some of the spectra of the substrates and products are shown in Figure 4.

Reagents and Instruments. Substituted benzylbis(dimethylglyoximate)(pyridine)cobalt(III) was prepared by the method of Schrauzer⁴¹ under basic conditions and recrystallized from 2-butanone. All complexes gave satisfactory elemental analyses. Iodine was the doubly sublimed reagent of Aldrich Co. Bis(pyridine)iodonium perchlorate,⁴² nitrosyl chloride,⁴³ and nitrosodurene⁴⁴ were prepared

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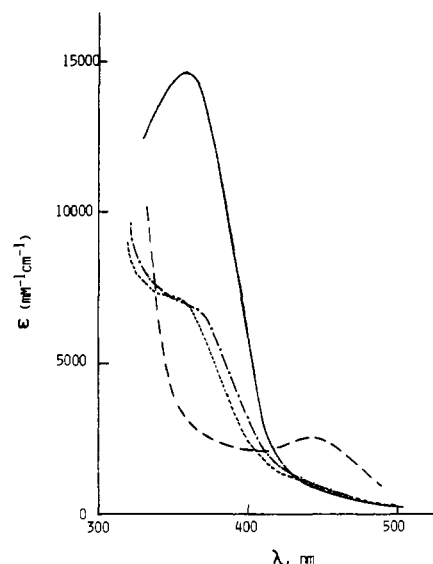


Figure 4. Absorption spectra of substrates and products: ---, $C_6H_5CH_2Co(DH)_2(py)$; ···, $CH_3C_6H_4CH_2Co(DH)_2(py)$; —·—, $NO_2C_6H_4CH_2Co(DH)_2(py)$; ····, $Co(DH)_2(py)I$ + benzyl iodide.

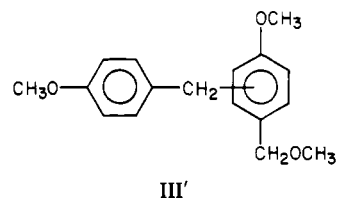
Table VI. Effect of Iodine on the Chemical Shift of Para-Substituted Benzylobis(dimethylglyoximate)(pyridine)cobalt(III)

| substrate | chem shift, ppm from Me_4Si | | | |
|-----------|-------------------------------|-------|----------------|-------|
| | original | | I_2 addition | |
| | CH_2 | DH-Me | CH_2 | DH-Me |
| Ic | 2.867 | 1.966 | 2.883 | 1.990 |
| Ib | 2.829 | 1.988 | 2.983 | 1.993 |
| Ia | 2.834 | 1.985 | 2.912 | 1.978 |
| Id | 2.734 | 2.005 | 2.851 | 2.005 |
| Ie | 2.721 | 2.004 | 2.843 | 2.042 |

according to the literature. Optically active (1-phenylethyl)bis(dimethylglyoximate)(pyridine)cobalt(III) was prepared from (+)-1-chlorophenylethane which was synthesized from (-)-1-phenylethanol (Norse Laboratories Inc.) by the literature method.⁴⁵ ($[\alpha]_D^{25} = +54.13^\circ$ (1 dm, neat), optical purity 43.2%).⁴⁶ Molar optical rotation of the cobalt complex ($[\alpha]_D^{25}$) was found to be -22° ($c = 2.32 \times 10^{-4}$, benzene) and was -51° after being corrected for the purity of the starting material. Authentic samples of the gas chromatographic analyses were prepared as follows. Dimethylglyoxime *O*-benzyl ether was prepared by stirring a mixture of dimethylglyoxime (1.7 mmol), sodium carbonate (0.6 mmol), and benzyl chloride (0.6 mmol) in 5 mL of dimethyl sulfoxide at 60 °C overnight, followed by working up with dichloromethane-water in 84% yield; mp 100–101 °C. Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.01; H, 6.85; N, 13.92. 1,2-Bis(*p*-methoxyphenyl)ethane was prepared by refluxing a mixture of *p*-methoxybenzyl chloride and sodium in benzene (75%). Anal. Found: C, 79.36; H, 7.48. Other materials were reagent grade. Kinetic studies were run with a Union SM 401

spectrophotometer. A gas chromatograph (Yanaco G8), a mass spectrometer (JMS-01SG), an NMR (Varian T60), and a polarimeter (Perkin-Elmer 241) were used for analyses.

Product Analyses. Complex I and 1.1 molar equiv of iodine were stirred in benzene at 40 °C. The reaction mixture was concentrated, the precipitate was filtered off, and the filtrate was refluxed with $NaOCH_3$ in methanol. The precipitate was an analytically pure iodo complex, II. The yield of anisole derivative was determined by gas chromatography. In the case of the *p*-methoxy complex the mixture after treatment by $NaOCH_3$ was chromatographed on silica gel with benzene-hexane as eluant to give a compound with m/e 271 in a yield of 18.7%, which is identified as a mixture of *p*-methoxy(*p*'-methoxybenzyl)benzyl methyl ethers, III' (NMR: 3.35 (3 H), 3.63 (2 H),



3.69 (3 H), 3.80 (3 H), 4.38 (2 H), 6.83–7.28 (7 H) ppm. Iodination of optically active cobalt complex (500 mg, 1.05 mmol) was carried out by stirring the complex with iodine (300 mg, 1.18 mmol) and tetrabutylammonium chloride (1.40 g, 5 mmol) in 50 mL of benzene for 14 h. The reaction mixture was chromatographed on silica gel with hexane as eluant to obtain 107 mg of organic product after removing the solvent, which contained 83 mg of phenylethyl chloride (56%). The chloride showed optical rotation ($[\alpha]_D^{25}$) being $1.78 \pm 0.16^\circ$ ($c = 1.24 \times 10^{-2}$, benzene). After correction for the purity of original chloride, the selectivity of iodination reaction was determined to be $3.0 \pm 0.3\%$.

Stoichiometry. Spectrophotometric titration was carried out at 370 nm by adding a benzene solution of iodine to three complexes of the concentration of 8.0×10^{-5} M.

Kinetic Study. The rate of iodination was measured spectrophotometrically in benzene after addition of a cobalt complex into a benzene solution of iodine and additives if necessary. The experiment with complex I in excess was measured at 500 nm. The reaction rate was influenced by the contact of the solution of iodine with a metallic species such as a hypodermic syringe and also by the aging of the benzene solution of iodine. It is probable that there is some impurity which influences the rate of reaction significantly. Kinetic measurements were carried out by using freshly prepared solutions without contact of metallic species with iodine solution to improve the reproducibility.

Treatment with Oxygen. Complex Ia (150 mg) in 10 mL of benzene- d_6 was stirred for 20 h at 40 °C under an oxygen atmosphere, and the 1H NMR spectrum of the solution was measured occasionally. No significant change was found in the spectra.

1H NMR Spectra of Iodination. 1H NMR spectra of complex Ia-e were measured at $-50^\circ C$ in $CDCl_3$, and the shift of each absorptions after the addition of iodine was determined. The results are summarized in Table VI.

Registry No. Ia, 27860-79-3; Ib, 36583-14-9; Ic, 42194-65-0; Id, 56669-78-4; Ie, 56498-37-4; If, 76157-49-8; II, 41659-64-7; III' (isomer 1), 76157-67-7; III' (isomer 2), 76156-68-8; III' (isomer 2), 76156-68-8; I₂, 7553-56-2; $PhCH(CH_3)Co(DH)_2(py)$, 76189-81-6; $CH_3O-C_6H_4CH_2I$, 70887-29-5; $C_6H_5CH_2I$, 620-05-3; $NO_2C_6H_4CH_2I$, 3145-86-6; dimethylglyoxime *O*-benzyl ether, 35584-80-6; 1,2-bis-(*p*-methoxyphenyl)ethane, 10543-21-2; dimethylglyoxime, 95-45-4; benzyl chloride, 100-44-7; *p*-methoxybenzyl chloride, 824-94-2.

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