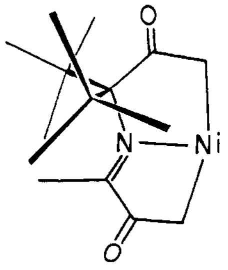
effect imposes more constraints on the α-alanate system than glycinate, thereby, if for no other reason, statistically reducing the stability of the complex. Since AIB possesses two C-methyl groups, considerable hindrance would occur in the carbinolamine form. Because of this the imine form predominates.

With pyruvate, hydrogen a is replaced by either the methyl group or the hydroxyl. In either case strong interference between this group and hydrogen b occurs in the carbinolamine. Thus, pyruvate complexes favor the imine. Zinc(II)-pyruvate-glycinate apparently can exist to an appreciable extent (30%) as the carbinolamine[4] owing to the more flexible coordination permitted by this metal ion. The interfering group can swing away from hydrogen b if a distortion from planar coordination is permitted.

The reduction in the intensity of ν_1 for nickel(II)-pyruvate-β-alanate reported in the preceding paper[7] suggests some carbinolamine formation. This result is consistent with the present conclusions since the more flexible six-membered ring permits hydrogen b to swing away from the interfering group even if planar coordination with the carboxylate oxygens occupying *trans* positions is required.

The imine of glyoxalate-AIB-nickel(II) has the structure



where substituent interference is minimized, but where ring strain nevertheless exists.

Reactivity of Hydrogen Atoms toward Some Cobalt(III) Complexes in Aqueous Solutions[1]

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Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. *Received October 8, 1965*

Abstract: Kinetic studies on the reduction of various cobalt(III) complexes by hydrogen atoms are described. The hydrogen atoms were generated by Co^{60} γ irradiation of the solutions and the rates of reaction with the cobalt(III) complexes determined by competition with the reaction with ethanol. Rate constants ranging from 3.3×10^{10} to 2.0×10^{7} M^{-1} sec^{-1} (at 26°) were determined for the reactions of H atoms with $Co(NH_3)_5I^{2+}$, $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5NCS^{2+}$, $Co(NH_3)_5(H\text{-fumarate})^{2+}$, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_3(NO_2)_3$, $Co(NH_3)_5NO_2^{2+}$, $Co(NH_3)_5CN^{2+}$, and $Co(CN)_6^{3-}$, along with upper limits for reactions with a number of other cobalt(III) complexes. In a number of cases the rates of reactions with the corresponding free ligands also were determined. The mechanisms of these reactions and the relation of the observed reactivity patterns for H atoms to those for other reductants are considered.

Recent studies[3-5] on the kinetics and mechanisms of inorganic electron-transfer reactions have included a number of systematic investigations on the reduction of cobalt(III) complexes (notably of the pentaamminecobalt(III) family) by various reducing agents including $Cr^{2+}(aq)$, $V^{2+}(aq)$, $Eu^{2+}(aq)$, $Cr(dipyridyl)_3^{2+}$, $Ru(NH_3)_6^{2+}$, and $Co(CN)_5^{3-}$. Among the objectives of these investigations have been the determination of whether electron transfer occurs by an inner- or outer-sphere mechanism and the elucidation and interpretation of the reactivity patterns, *e.g.*, that of a given reductant toward a series of different pentaamminecobalt(III) complexes. Similarities as well as differences among the reactivity patterns of the various reductants were found, some of which apparently are related to whether the electron-transfer reactions are of the inner- or outer-sphere type. The significance of these reactivity patterns, particularly for inner-sphere reactions, is, however, far from completely understood and their elucidation calls for further work.

In this context it appeared of interest to examine the kinetics of the reduction of a variety of pentaammine and related cobalt(III) complexes by still another reducing agent of somewhat different, but not unrelated, properties, namely, atomic hydrogen. At the time that this investigation was undertaken only a few such measurements had been reported,[6] based on a very indirect method which yielded only relative rate constants. While this work was in progress, two other papers[7,8] appeared reporting further kinetic measurements on such reactions. In view of the incomplete scope of

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[1] Support of this research through a grant from the National Science Foundation and through a grant to the University of Chicago from the Advanced Research Projects Agency is gratefully acknowledged.

[2] Department of Physical Chemistry, Hebrew University, Jerusalem, Israel.

[3] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[4] J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964).

[5] J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963). J. Halpern and S. Nakamura, "Proceedings of the 8th Conference on Coordination Chemistry, Vienna," Springer Verlag, Berlin, 1964, p 271.

[6] E. Collinson, F. S. Dainton, B. Mile, S. Tazuke, and D. R. Smith, *Nature*, **198**, 26 (1963).

[7] G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1391 (1965).

[8] M. Anbar and D. Meyerstein, *Nature*, **206**, 818 (1965).

these investigations and of some discrepancies between the two sets of results which were obtained by quite different experimental methods, it appeared worthwhile to complete and extend the present investigation. The results reported here include rate constants, determined by yet another method, for some of the reactions previously investigated, as well as for the reactions of hydrogen atoms with a number of other cobalt(III) complexes and, in some cases, with the corresponding free ligands.

Experimental Section

Materials. The cobalt(III) complexes were prepared by the procedures previously described.[3] Other chemicals were analytical grade reagents. Triple distilled water was used to prepare the solutions.

Procedure. The rates of reaction of H atoms with the cobalt(III) complexes were determined by a competition method based on the competing reactions of the H atoms with ethanol and with the cobalt(III) complex.

The H atoms were generated by γ irradiation of the solutions using a Co^{60} source.[9] The dose rate was determined with the Fricke dosimeter using $G(Fe^{+3}) = 15.5$ and $\epsilon_{3050} = 2200$ at 25°, a correction being applied for other temperatures. Solutions were prepared by the syringe technique[10] using redistilled argon to force the solutions into the syringes; dilutions were made by means of microsyringes.[11] Irradiation was carried out in the absence of a gas phase. Two radiation sources, having dose rates of 1×10^{19} and 1.5×10^{18} ev $l.^{-1}$ sec^{-1}, were used and gave consistent results. The total dose in each experiment was about 1.3×10^{20} ev $l.^{-1}$.

Unless otherwise indicated, the reaction solutions contained 0.1 M $HClO_4$ which, at this concentration, apparently is inert to the species produced by the irradiation.[12] All kinetic measurements were made at 26 ± 1°.

The absorption of γ radiation by water generates various radical and molecular species, notably $e^-(aq)$, H, OH, H_2, H_2O_2, H^+, and OH^-.[13]

In acidic solutions $e^-(aq)$ is converted to H atoms[14] by reaction with H^+ with a rate constant of 2×10^{10} M^{-1} sec^{-1}.[15] The equilibrium, $H^+ + OH^- \rightleftarrows H_2O$, is sufficiently rapidly achieved so that under conditions of low-intensity steady radiolysis the effects of the radiation-produced H^+ and OH^- can be neglected, particularly in solutions containing added acid or base. The species whose effects are to be considered are thus: H, OH, H_2O_2, and H_2.

Our method for the determination of the rate constants of the reactions of H atoms with the cobalt(III) complexes was essentially that first used by Baxendale and Smithies[16] and subsequently by many other workers.[17] Ethanol, in known concentrations, was added to react[18,19] with the H atoms and OH radicals according to eq 1 and 2. If all the hydrated electrons produced by the radiolysis

$$H + CH_3CH_2OH \longrightarrow H_2 + CH_3CHOH \qquad (1)$$

$$OH + CH_3CH_2OH \longrightarrow H_2O + CH_3CHOH \qquad (2)$$

are converted to H atoms by reaction 3 and subsequently react with

$$e^-(aq) + H^+ \longrightarrow H \qquad (3)$$

ethanol according to (1), then the total experimental yield of H_2, denoted as $G(H_2)$ (and expressed in molecules per 100 ev), is given by

$$G(H_2) = G_e + G_H + G_{H_2} \qquad (4)$$

where G_e, G_H, and G_{H_2} are the primary radiation-produced yields of $e^-(aq)$, H, and H_2, respectively.

If another solute, X, is added, which also reacts with H atoms, but without producing H_2, then the total yield of H_2, *i.e.*, $G(H_2)$, will be reduced to an extent which depends on the ratio of the concentrations of X to C_2H_5OH in accord with

$$\frac{1}{G(H_2) - G_{H_2}} = \frac{1}{G(H)} + \frac{1}{G(H)}\left[\frac{k_{H+X}}{k_1}\frac{[X]}{[C_2H_5OH]}\right] \qquad (5)$$

where k_1 is the rate constant of reaction 1, k_{H+X} the rate constant for the reaction of H with X, and $G(H)$ the total yield of H atoms for which the two solutes compete.

In 0.1 M $HClO_4$ where all the hydrated electrons are converted to H atoms, $G(H) = G_e + G_H$. In a few experiments in near-neutral solutions where quantitative conversion of $e^-(aq)$ to H is no longer assured, acetone was added to scavenge the electrons according to[14]

$$e^-(aq) + CH_3COCH_3 \longrightarrow (CH_3COCH_3)^- \qquad (6)$$

Under these conditions eq 5 is still valid, but now $G(H) = G_H$ (≈ 0.55).

Values of k_{H+X} for the reactions of H atoms with various cobalt(III) complexes were determined, using eq 5, from measurements of $G(H_2)$ at various $[X]/[C_2H_5OH]$ ratios. Values of $[X]/[C_2H_5OH]$ were corrected for solute depletion during irradiation, the correction generally amounting to less than 10%. The H_2 produced during irradiation was separated from the solution with a Van Slyke apparatus and determined gas chromatographically using an Aerograph 660 gas chromatograph and a 13-X molecular sieve column.

The G values used in our calculations were: $G_{H_2} = 0.43$ in 0.1 M $HClO_4$ solution; $G_{H_2} = 0.40$ and 0.34 in neutral solutions containing 2×10^{-3} and 2.5-5 $\times 10^{-2}$ M acetone, respectively.

Results

Effect of Ethanol on $G(H_2)$. The dependence of $G(H_2)$ in 0.1 M $HClO_4$ on the concentration of ethanol, in the absence of other solutes, was determined experimentally. The results are shown in Figure 1 and are in accord with those of other workers.[18,19] The slight increase in $G(H_2)$ with ethanol concentration is probably due in part to an increase in G_H and, possibly in part, to the effects of impurities which compete more effectively for H atoms with ethanol at low concentrations of the latter. The values of $G(H_2)$ corresponding to the solid curve in Figure 1 were used in the subsequent determinations.

Competition of C_2H_5OH and O_2 for H Atoms. Our method for determination of the absolute rate constants for the reactions of H with cobalt(III) complexes depends on a knowledge of k_1. Unfortunately, k_1 has not yet been directly determined. Many previously reported "absolute" rate constants for reactions of H atoms are based on comparison with k_{H+O_2}, which in turn is somewhat uncertain but is at least approximately known. Our method was therefore "calibrated" by determining k_1 relative to k_{H+O_2} by measuring $G(H_2)$ for solutions containing various $[O_2]/[C_2H_5OH]$ ratios. The results are shown in Figure 2 and yield $k_{H+O_2}/k_1 = 520 \pm 80$ (based on $G_{H_2} = 0.43$).

There is still some uncertainty about the value of k_{H+O_2}. Schwarz[20] has reported a value of $(2.0 \pm 0.4) \times 10^7$ M^{-1} sec^{-1} for $k_{H+Fe^{2+}}$. Allen and Rothschild[21] reported $k_{H+O_2}/k_{H+Fe^{2+}} = (1.2 \pm 0.3) \times 10^3$ in 0.8 N H_2SO_4 (and a somewhat higher value at pH

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[9] We are grateful to Dr. L. E. Kevan for the use of the Co^{60} sources.

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[13] M. S. Matheson and J. Rabani, *ibid.*, **69**, 1324 (1965), and references cited therein.

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[18] C. Lifshitz and G. Stein, *J. Chem. Soc.*, 3706 (1962).

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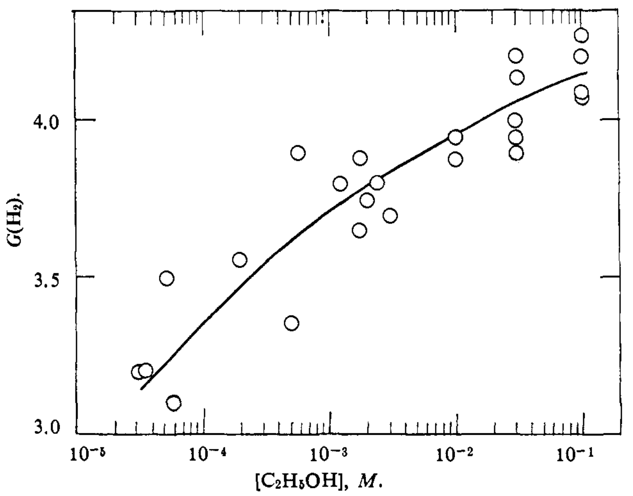

Figure 1. Dependence of $G(H_2)$ in 0.1 M $HClO_4$ on the ethanol concentration.

2.1). Combination of these measurements yields $k_{H+O_2} = (2.4 \pm 1.1) \times 10^{10}\ M^{-1}\ sec^{-1}$. An attempted direct determination[22] of k_{H+O_2} using pulse radiolysis techniques yielded $k_{H+O_2} = 2.1 \times 10^{10}\ M^{-1}\ sec^{-1}$. Other indirect determinations[22,23] have yielded values of 1.2×10^{10}, 1.9×10^{10}, and $2.6 \times 10^{10}\ M^{-1}\ sec^{-1}$ for k_{H+O_2}. Using the value $k_{H+O_2} = 2.0 \times 10^{10}\ M^{-1}\ sec^{-1}$, the results in Figure 2 yield $k_1 = 3.8 \times 10^7\ M^{-1}\ sec^{-1}$. It should be noted that this value and all the other rate constants reported in this paper are subject to modification in the light of future re-evaluation of k_{H+O_2}.

Reactions of H Atoms with Cobalt(III) Complexes. The results of our measurements on the rates of reaction of H atoms with various cobalt(III) complexes are summarized in Table I. Typical data, plotted in accord with eq 5, are shown in Figure 3. Rate constants computed from the slopes of such plots using eq 5 are summarized in Table III.

The reactions of a number of the complexes with H atoms were too slow for the rate constants to be reliably estimated by the method used, and in these cases only upper limits for the rate constants could be established (see Table II). These complexes include $Co(NH_3)_6^{3+}$, $Co(NH_3)_5OH_2^{3+}$, $Co(NH_3)_5F^{2+}$, $Co(NH_3)_5OAc^{2+}$, and $Co(NH_3)_5PO_4$. Slight decreases in $G(H_2)$ with increasing [Co(III)]/[ethanol] ratios were noted in most of these cases, the decreases for $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5OH_2^{3+}$ being larger than could be accounted for by a decrease in G(H) owing to reaction of the cobalt(III) complex with e^-(aq). Nevertheless, the scavenging efficiencies of these complexes for H atoms are so low that the possibility of contributions from impurities cannot be excluded, and in our view only the significance of upper limits should be assigned to the rate constants for these systems.

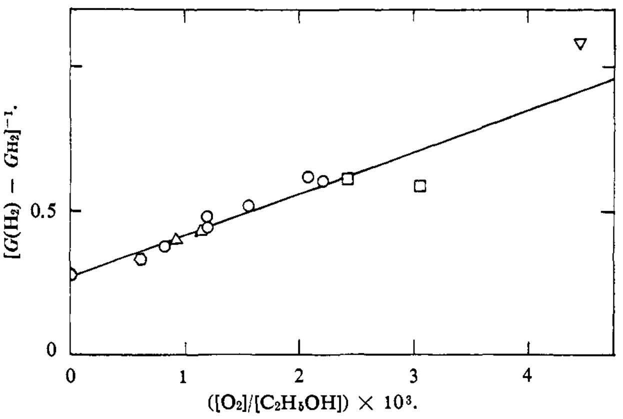

Figure 2. Competition between ethanol and oxygen for H atoms in 0.1 M $HClO_4$. Ethanol concentrations (M): ▽, 0.05; □, 0.08; O, 0.10; △, 0.20; O, 0.40.

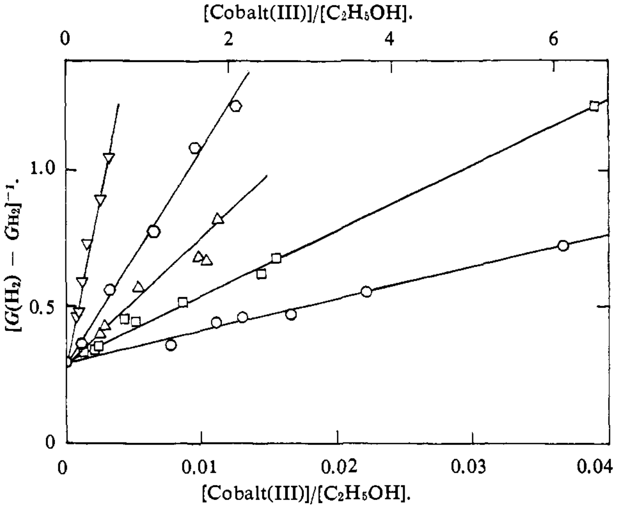

Figure 3. Typical plots according to eq 5 showing competition between ethanol and various cobalt(III) complexes for H atoms (based on data in Table I): O, $Co(NH_3)_5Cl^{2+}$; □, $Co(CN)_6^{3-}$; △, $Co(NH_3)_5NCS^{2+}$; O, $Co(NH_3)_5CN^{2+}$; ▽, $Co(NH_3)_5I^{2+}$. Upper scale applies to $Co(NH_3)_5CN^{2+}$ and $Co(CN)_6^{3-}$, lower scale to the other complexes.

The values of the rate constants for the reactions of H with $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5F^{2+}$ determined by Navon and Stein[7] and by Anbar and Meyerstein[8] are consistent with (and only slightly below) our upper limits for these rate constants. Their reported values of 1.9×10^6 and $1.6 \times 10^6\ M^{-1}\ sec^{-1}$, respectively, for $k_{H+Co(NH_3)_6^{3+}}$ are in excess of our estimated upper limit for this rate constant; for the reasons already given we are inclined to suspect impurity effects in these cases.

The high value of $G(H_2)$ (=1.23) observed for a solution containing $4.4 \times 10^{-4}\ M$ $Co(NH_3)_5OAc^{2+}$, *in the absence of ethanol*, may reflect hydrogen abstraction from the acetate ligand by H atoms. No indication of hydrogen abstraction was found with $Co(NH_3)_5F^{2+}$ ($G(H_2)$ = 0.50 in the absence of ethanol) and only a slight indication with $Co(NH_3)_5OOClF_3^{2+}$ ($G(H_2)$ = 0.64 in the absence of ethanol), which may reflect reactions with impurities rather than with the complex. Hydrogen abstraction by H atoms from $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5OH_2^{3+}$ has previously been ruled out by Katakis and Allen.[24]

The reactivity of H atoms toward the other cobalt(III) complexes listed in Tables I and II were sufficiently high for the rate constants to be determined reliably by the method used. These rate constants ranged from 3.3×10^{10} for $k_{H+Co(NH_3)_5I^{2+}}$ to 2.0×10^7 for

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(22) S. Gordon, E. J. Hart, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1262 (1964).

(23) J. K. Thomas, *ibid.*, **67**, 2593 (1963); H. Fricke and J. K. Thomas, *Radiation Res. Suppl.*, **4**, 35 (1964); J. P. Sweet and J. K. Thomas, *J. Phys. Chem.*, **68**, 1363 (1964).

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Table I. Reactions of H Atoms with Cobalt(III) Complexes[a]

Co(III) compd	[Ethanol], *M*	$\frac{[\text{Complex}]}{[\text{Ethanol}]}$	$G(H_2)$
$[Co(NH_3)_5Cl]Cl_2$	1.0×10^{-2}	7.7×10^{3}	3.23
	2.0×10^{-2}	1.11×10^{-2}	2.67
	1.0×10^{-2}	1.66×10^{-2}	2.56
	1.0×10^{-2}	3.67×10^{-2}	1.82
	5.0×10^{-3}	4.45×10^{-2}	1.67
	6.0×10^{-4}	6.1×10^{-1}	0.51
$[Co(NH_3)_5Cl](ClO_4)_2$	1.0×10^{-2}	1.30×10^{-2}	2.59
	1.0×10^{-2}	2.21×10^{-2}	2.23
$[Co(NH_3)_5Br]Br_2$	1.0×10^{-1}	1.11×10^{-3}	3.05
	1.5×10^{-1}	1.69×10^{-3}	2.77
	1.0×10^{-1}	2.00×10^{-3}	2.50
	9.5×10^{-2}	3.75×10^{-3}	1.86
	5.7×10^{-2}	4.8×10^{-3}	1.90
	9.0×10^{-2}	5.7×10^{-3}	1.62
	0	∞	0.38[b]
$[Co(NH_3)_5Br](ClO_4)_2$	1.0×10^{-1}	1.99×10^{-3}	2.78
$[Co(NH_3)_5I]Cl_2$	2.7×10^{-1}	7.4×10^{-4}	2.57
	1.0×10^{-1}	1.1×10^{-3}	2.55
	1.0×10^{-1}	1.2×10^{-3}	2.12
	2.8×10^{-1}	1.5×10^{-3}	1.80
	1.0×10^{-1}	2.5×10^{-3}	1.90
	3.0×10^{-1}	2.6×10^{-3}	1.55
	9.3×10^{-2}	3.2×10^{-3}	1.39
$[Co(NH_3)_5N_3](ClO_4)_2$	8.0×10^{-3}	3.0×10^{-2}	2.34
	8.0×10^{-3}	6.7×10^{-2}	1.64
	2.4×10^{-2}	8.1×10^{-2}	1.44
	8.0×10^{-3}	1.36×10^{-1}	1.03
$[Co(NH_3)_5NCS](ClO_4)_2$	3.0×10^{-2}	2.43×10^{-3}	3.30
	6.0×10^{-2}	2.69×10^{-3}	2.99
	3.0×10^{-2}	2.82×10^{-3}	2.74
	3.0×10^{-2}	5.4×10^{-3}	2.18
	3.0×10^{-2}	9.8×10^{-3}	1.92
	1.5×10^{-2}	1.04×10^{-2}	1.93
	3.0×10^{-2}	1.11×10^{-2}	1.63
	0	∞	0.46[c]
$[Co(NH_3)_5CN]Cl_2$	6.0×10^{-4}	0.19	3.23
$[Co(NH_3)_5CN](ClO_4)_2$	3.4×10^{-3}	0.53	2.22
	1.7×10^{-3}	1.08	1.73
	1.7×10^{-3}	1.57	1.35
	1.7×10^{-3}	2.10	1.24
$[Co(NH_3)_5NO_2](ClO_4)_2$	4.0×10^{-3}	1.07×10^{-1}	3.38
	2.0×10^{-3}	2.14×10^{-1}	2.35
	4.0×10^{-3}	3.3×10^{-1}	1.97
	2.0×10^{-3}	4.8×10^{-1}	1.65
	4.0×10^{-5}	19	0.42
$[Co(NH_3)_5(NO_2)_3]$	4.0×10^{-3}	6.5×10^{-3}	3.30
	4.0×10^{-3}	1.32×10^{-2}	2.83
	4.0×10^{-3}	2.8×10^{-2}	2.73
	4.0×10^{-3}	8.0×10^{-2}	1.78
	2.0×10^{-3}	5.2×10^{-2}	1.90
	4.0×10^{-3}	1.63×10^{-1}	1.33
	2.0×10^{-3}	5.5×10^{-1}	0.71
	5.0×10^{-3}	22	0.45
$Na_3[Co(CN)_6]$	2.4×10^{-3}	1.78×10^{-1}	3.32
	2.4×10^{-3}	3.6×10^{-1}	3.42
	1.2×10^{-3}	7.1×10^{-1}	2.66
	2.7×10^{-3}	8.5×10^{-1}	2.68
	1.2×10^{-3}	1.43	2.40
	1.2×10^{-3}	2.43	2.08
$K_3[Co(CN)_6]$	1.0×10^{-3}	2.60	1.91
	2.0×10^{-3}	6.5	1.24
	1.0×10^{-3}	9.1	1.08
	0	∞	0.37[d]
$[Co(NH_3)_6](ClO_4)_3$	3.0×10^{-3}	0.95	3.2
	5.7×10^{-4}	9.1	2.9
	3.0×10^{-5}	79	2.5
$[Co(NH_3)_5H_2O](ClO_4)_3$	5.7×10^{-4}	18	2.32
	1.5×10^{-4}	42	2.13
$[Co(NH_3)_5F](ClO_4)_2$	1.1×10^{-3}	3.0	3.10
	6.0×10^{-4}	8.9	2.97
	1.0×10^{-3}	10.6	2.83
	0	∞	0.50[e]
$[Co(NH_3)_5OAc](ClO_4)_2$	1.0×10^{-2}	8.7×10^{-2}	3.80
	5.0×10^{-4}	4.1	3.15
	0	∞	1.23[f]
$[Co(NH_3)_5OOCCF_3]-$ $(ClO_4)_2$	1.0×10^{-3}	4.9	3.48
	5.0×10^{-5}	54	2.72
	2.3×10^{-5}	75	2.60
	0	∞	0.64[g]
$[Co(NH_3)_5PO_4]$	2.0×10^{-4}	7.0	3.20
$[Co(NH_3)_5($*trans*-$OOCCH=CHCOOH)](ClO_4)_2$	4.0×10^{-2}	2.0×10^{-3}	3.02
	2.0×10^{-2}	1.2×10^{-2}	1.94
	1.0×10^{-2}	2.3×10^{-2}	1.31
	4.0×10^{-3}	6.1×10^{-2}	0.73
	5.0×10^{-5}	30	0.42

[a] All measurements at 26 ± 1° in 0.1 *M* $HClO_4$ unless otherwise noted. [b] 2.95×10^{-4} *M* $[Co(NH_3)_4Br]Br_2$. [c] 1.7×10^{-4} *M* $[Co(NH_3)_5NCS](ClO_4)_2$; 1.39×10^{-4} *M* KBr. [d] 1.0×10^{-2} $K_3[Co(CN)_6]$; 5×10^{-5} KBr. [e] 8×10^{-4} *M* $[Co(NH_3)_5F](ClO_4)_2$; 1×10^{-4} *M* KBr. [f] 4.4×10^{-4} *M* $[Co(NH_3)_5OAc](ClO_4)_2$. [g] 2×10^{-3} *M* $[Co(NH_3)_5OOCCF_3](ClO_4)_2$; 1×10^{-4} *M* KBr.

Table II. Reactions of H Atoms with Free Ligands

Ligand	[Ethanol], *M*	$\frac{[\text{Ligand}]}{[\text{Ethanol}]}$	$G(H_2)$[a]
NO_2^-[b]	2.3×10^{-2}	1.09×10^{-2}	0.76
	2.2×10^{-2}	2.85×10^{-2}	0.60
	8.0×10^{-3}	3.75×10^{-2}	0.57
	7.7×10^{-3}	1.00×10^{-1}	0.49
	0	∞[c]	0.35
HNO_2[d]	8.0×10^{-3}	2.4×10^{-2}	2.45
	1.6×10^{-2}	4.9×10^{-2}	1.92
	8.0×10^{-3}	9.8×10^{-2}	1.40
	0	∞	0.44[e]
N_3^-[f]	2.0×10^{-1}	3.6×10^{-3}	0.65
	2.0×10^{-1}	7.3×10^{-3}	0.61
N_3^-[g]	1.0×10^{-1}	7.2×10^{-3}	0.58
	1.0×10^{-1}	1.46×10^{-2}	0.53
	5.0×10^{-2}	3.05×10^{-2}	0.40
	5.0×10^{-2}	3.84×10^{-2}	0.40
	5.0×10^{-2}	1.19×10^{-1}	0.34
HN_3[h]	2.0×10^{-1}	2.40×10^{-2}	3.97
	1.0×10^{-1}	5.76×10^{-2}	3.42
	2.5×10^{-2}	1.16×10^{-1}	3.06
	2.5×10^{-2}	2.60×10^{-1}	2.07
	2.5×10^{-2}	4.50×10^{-1}	1.65
$[\text{Fumarate}]^{2-}$[i]	5.0×10^{-2}	7.9×10^{-2}	0.40
$[\text{H-fumarate}]^-$[j]	5.0×10^{-2}	1.35×10^{-2}	0.51
	5.0×10^{-2}	2.3×10^{-2}	0.50
	5.0×10^{-2}	1.7×10^{-1}	0.37

[a] Measured $G(H_2)$ values for media used (other than 0.1 *M* $HClO_4$) when no ligand present: $G(H_2) = 0.88$ for neutral solution containing 5×10^{-2} *M* ethanol and 2.5×10^{-2} *M* acetone; $G(H_2) = 0.99$ for solution containing 5×10^{-3} *M* $NaHCO_3$, 8×10^{-3} *M* ethanol, and 2.2×10^{-3} *M* acetone. [b] $NaNO_2$ in 5×10^{-3} *M* $NaHCO_3$ containing 2.2×10^{-3} *M* acetone. [c] 8×10^{-4} *M* $NaNO_2$. [d] In 0.1 *M* $HClO_4$. [e] 8×10^{-4} *M* HNO_2. [f] NaN_3 in 5.0×10^{-2} *M* acetone; no added acid. [g] NaN_3 in 2.5×10^{-2} *M* acetone; no added acid. [h] In 0.1 *M* $HClO_4$. [i] Sodium fumarate in 6×10^{-3} *M* NaOH and 2.7×10^{-2} *M* acetone. [j] In 2.7×10^{-2} *M* acetone; total ligand concentration includes 90% H-fumarate⁻ and 10% fumarate²⁻.

$k_{H+Co(CN)_6^{3-}}$. Our determinations yield for the ratios, $k_{H+Co(NH_3)_5Cl^{2+}}:k_{H+Co(NH_3)_5Br^{2+}}:k_{H+Co(NH_3)_5I^{2+}}$ the values 1:8.8:21, in reasonable agreement with the corresponding ratios 1:4.5:13.7 (at pH 4–6) reported by Anbar and Meyerstein[8] and 1:6.3:45 (in neutral solution) reported by Navon and Stein.[7] There are, however, discrepancies of up to a factor of ten between our absolute rate constants and the earlier ones for these compounds as well as for $k_{H+Co(NH_3)_5N_3^{2+}}$ and $k_{H+Co(NH_3)_5CN^{2+}}$. These discrepancies are probably not

Table III. Summary of Rate Constants

Substrate	$k_{\mathrm{H+substrate}}$,[a] M^{-1} sec^{-1}
$Co(NH_3)_5I^{2+}$	$(3.3 \pm 0.8) \times 10^{10}$
$Co(NH_3)_5Br^{2+}$	$(1.4 \pm 0.2) \times 10^{10}$
$Co(NH_3)_5NCS^{2+}$	$(6.3 \pm 0.7) \times 10^{9}$
$Co(NH_3)_5(\text{H-fumarate})^{2+}$	$(6.1 \pm 1.0) \times 10^{9}$
$Co(NH_3)_5Cl^{2+}$	$(1.6 \pm 0.2) \times 10^{9}$
$Co(NH_3)_5N_3^{2+}$	$(1.1 \pm 0.3) \times 10^{9}$
$Co(NH_3)_3(NO_2)_3$	$(9.6 \pm 1.3) \times 10^{8}$
$Co(NH_3)_5NO_2^{2+}$	$(1.6 \pm 0.2) \times 10^{8}$
$Co(NH_3)_5CN^{2+}$	$(6.1 \pm 0.8) \times 10^{7}$
$Co(CN)_6^{3-}$	$(2.0 \pm 0.3) \times 10^{7}$
$Co(NH_3)_5F^{2+}$	$\lesssim 2.0 \times 10^{6}$
$Co(NH_3)_5OAc^{2+}$	$\lesssim 1.3 \times 10^{6}$
$Co(NH_3)_5OH_2^{3+}$	$\lesssim 1.0 \times 10^{6}$
$Co(NH_3)_5PO_4$	$\lesssim 6.7 \times 10^{5}$
$Co(NH_3)_5OOCCF_3^{2+}$	$\lesssim 2.7 \times 10^{5}$
$Co(NH_3)_6^{3+}$	$\lesssim 1.3 \times 10^{5}$
NO_2^-	$(2.4 \pm 0.4) \times 10^{9}$
HNO_2	$(1.0 \pm 0.2) \times 10^{9}$
N_3^-	$(7.3 \pm 0.8) \times 10^{9}$
HN_3	$(1.6 \pm 0.1) \times 10^{8}$
H-fumarate$^-$	$\sim 5 \times 10^{9}$

[a] At 26 ± 1°; other conditions given in Tables I and II.

outside the uncertainty of the diffusion model on which the determinations of Navon and Stein are based and undoubtedly also arise in part from the use by Anbar and Meyerstein of a value of $k_{\mathrm{H+2\text{-}D\text{-}propanol}}$ which is too low, being based in turn on $k_{\mathrm{H+O_2}} = 1.9 \times 10^9$ M^{-1} sec^{-1}. The other rate constants listed in Table II have not previously been determined.

In a number of cases including $Co(NH_3)_5NO_2^{2+}$, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, $Co(NH_3)_5NCS^{2+}$, $Co(NH_3)_5$-(*trans*-OOCCH=CHCOOH)$^{2+}$, and $Co(CN)_6^{3-}$, it was established (Table I) that $G(H_2)$ approached a limiting value of ~0.4 ($\sim G_{H_2}$) with increasing [cobalt(III)]/[ethanol] ratio. It thus appears that, except for the case of $Co(NH_3)_5OAc^{2+}$ referred to earlier, H atoms react with these complexes by reduction rather than by hydrogen abstraction.

In addition to the cobalt(III) complexes, the reaction solutions generally contained one or more of the following anions: ClO_4^-, Br^-, Cl^-. At the concentrations used ClO_4^- is apparently inert to all the species present in the solution. Br^- and Cl^- are unreactive toward H atoms but susceptible to oxidation (to Br and Cl, respectively) by OH.[25] Scavenging of OH radicals by ethanol, however, is sufficiently efficient under the conditions of our rate constant measurements to prevent this ($k_{\mathrm{OH+ethanol}} = 2 \times 10^9$ M^{-1} sec^{-1}).[26] In certain experiments, designed to determine whether H atoms react by hydrogen abstraction from the cobalt complexes, ethanol was absent and KBr was deliberately added to scavenge the OH radicals.

Reactions of H Atoms with Free Ligands. In a number of cases it was considered important to determine the reactivity of H atoms toward the free ligands because of the possibility that the free ligand is produced under the conditions of the reaction by hydrolysis or decomposition of the cobalt complexes. In certain cases it was also of some interest to determine the relative reactivities of the free ligand and the complex. The results of our measurements are summarized in Tables III and II.

The value of 2.4×10^9 M^{-1} sec^{-1} for $k_{\mathrm{H+NO_2^-}}$ agrees with several earlier determinations of this rate constant when normalized to the value of $k_{\mathrm{H+CH_3CH_2OH}}$ ($= 3.8 \times 10^7$) used by us.[17a,c] Our results further indicate little differences between the reactivities of NO_2^- and HNO_2 toward H atoms. Reaction of H atoms with HNO_2 apparently does not involve hydrogen abstraction since a 0.1 M $HClO_4$ solution containing 8×10^{-4} M HNO_2, in the absence of ethanol, yielded a value of $G(H_2) = 0.44$ ($\sim G_{H_2}$). It is also of interest that the reactivity of $Co(NH_3)_5NO_2^{2+}$ toward H atoms is significantly lower than that of either NO_2^- or HNO_2 (Table II). In contrast to this, the reactivity of $Co(NH_3)_5N_3^{2+}$ was found to be intermediate between the reactivities of N_3^- and HN_3. The results for fumarate are less precise but suggest that the reactivities of $HOOCCH{=}CHCOO^-$ and $^-OOCCH{=}CHCOO^-$ toward H atoms are similar to each other and to that of $Co(NH_3)_5(OOCCH{=}CHCOOH)^{2+}$.

Discussion

While the products of reaction of H atoms with the cobalt complexes were not established in these studies, it appears that, with the possible exceptions of $Co(NH_3)_5NO_2^{2+}$, $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_5(OOCCH{=}CHCOOH)^{2+}$, and $Co(NH_3)_5NCS^{2+}$, which will be referred to separately, the ligands of the complex are inert toward H atoms and the reactions with H atoms involve reduction of the cobalt(III). This is also supported by the general agreement of our rate constants (and those of Anbar and Meyerstein[8]) with the rate constants determined by Navon and Stein[7] for the formation of cobalt(II) by reaction of H atoms with cobalt(III) complexes.

The nature of the reductant, its low reactivity toward $Co(NH_3)_6^{3+}$, and the very drastic solvation change associated with the direct (outer-sphere) oxidation of H atoms to H_3O^+ make it seem very likely that the observed reactions of H atoms with the cobalt(III) complexes occur by a mechanism analogous to the inner-sphere (bridged) reduction of cobalt(III) complexes by Cr^{2+}, $Co(CN)_5^{3-}$, etc.,[3-5] and involving attack of the H atom on the anionic ligand,[27] *i.e.*,

$$(NH_3)_5Co^{III}X^- + H \longrightarrow [(NH_3)_5Co^{II}XH] \longrightarrow Co^{II} + HX\ (\text{or } H^+ + X^-) + 5NH_3 \quad (7)$$

The reactivity pattern toward different cobalt(III) complexes determined above for H atoms is not sufficiently distinctive, when compared to those for other reductants,[3-5,28] to either support or refute this view, except to the extent that it does not appear to resemble the common reactivity pattern exhibited by several different outer-sphere oxidants and thus indirectly favors an inner-sphere mechanism. Inner-sphere mechanisms involving transfer of bridging ligands have also been proposed for the reduction of metal salts by organic free radicals.[29]

It is of some interest to compare the reactivity order of H atoms toward the halopentaamminecobalt(III) complexes, *i.e.*, $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} >$

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$Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$, with that for other inner-sphere reductants. The order is the same as that observed for Cr^{2+} [28] and $Co(CN)_5^{3-}$ [5] as reductants but the reverse of that observed for Eu^{2+} [3] and Fe^{2+} [30] which are also believed to reduce these cobalt(III) complexes by inner-sphere mechanisms and which exhibit the reactivity order, $Co(NH_3)_5F^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5I^{2-}$. Since the inner-sphere mechanism involves transfer of the bridging ligand from the cobalt to the reductant, *i.e.*

$$\text{Co–X} + \text{red} \longrightarrow \text{Co} + \text{X–red}$$

it is to be expected that the reactivity order when X is varied will be influenced by the variation of the strengths of both the bond being broken (Co–X) and the bond being formed (X–red). For the oxidants and reductants in question the trend is almost certainly for both bond strengths to increase in the order I < Br < Cl < F. It might further be expected that for highly reactive reductants the influence of bond making in the transition state is of less importance than bond breaking, and hence that the reactivity order should follow the sequence determined by the strength of the bond being broken, *i.e.*, $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$. For reductants of low reactivity, on the other hand, stabilization of the transition state by bond making to the reductant is expected to assume greater importance, and the reactivity order should thus be influenced to a greater degree by the strength of the bond being formed, *i.e.*, F > Cl > Br > I. Put in a somewhat different way, this is equivalent to saying that in highly exo-free energetic reactions the transition state tends to resemble the reactants, whereas in endo-free energetic reactions it tends to resemble the product. The observed reactivity orders of the different reductants toward the halopentaammine complexes are consistent with this interpretation when considered in the light of the absolute reactivities of these reductants which follow the order: H (1.6×10^9) > $Co(CN)_5^{3-}$ (2×10^7) > Cr^{2+} (2.6×10^6) > Eu^{2+} (3.9×10^2) > Fe^{2+} (1.4×10^{-3}), the values in parentheses being the rate constants (in M^{-1} sec^{-1} at 25°) for reaction with $Co(NH_3)_5Cl^{2+}$.

Finally some comment is in order on those complexes that contain ligands which are reactive toward H atoms in the uncomplexed state. In these cases the possibility must be considered that the reactivity of the complex toward H atoms is essentially that of the ligand, influenced only to a minor degree by the presence of the reducible cobalt(III) center, and hence that these reactions differ in a rather fundamental way from those of the other cobalt(III) complexes. While the observed comparisons of the reactivities of several of the complexes and the corresponding free ligands (notably fumarate, NO_2^-, and N_3^-) are consistent with this view, they do not rule out some influence of the cobalt(III) center, and further investigations directed at elucidating this important point would appear to be called for.

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Electronic Character of Metal–Anion Bonds

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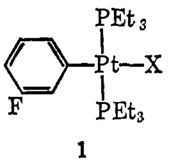
Abstract: The F^{19} nmr shielding parameters of *m*- and *p*-fluorophenylplatinum(II) complexes provide a criterion of the electronic characteristics of other metal–ligand bonds in the compounds. The σ-donor characteristics measured in this way parallel the basicities of the anions involved. The CN^-, $C_6H_5C{\equiv}C^-$, and $SnCl_3^-$ ions are strong π acceptors, but the halide ions have a net π-donor effect.

The electronic interaction between a metal ion and a coordinated ligand has been studied by many physical techniques.[1] The electronic spectra of ionic complexes[2] and the infrared spectra of octahedral metal carbonyls[3] have been particularly useful in assessing the nature of the metal–ligand bond. In complexes of the type $XMn(CO)_5$, the C=O stretching frequency of the carbonyl *trans* to the anionic ligand X can be related to the σ-donor and π-acceptor character of the Mn–X bond. A recent communication[4] described the use of F^{19} nmr shielding parameters of fluorophenylplatinum complexes (**1** and **2**) to study the Pt–X bond. A fuller description of this technique is reported here.



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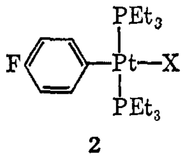

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The F^{19} shielding parameter of a monosubstituted fluorobenzene is a very sensitive criterion of the electronic effect of the substituent.[5,6] An inductive elec-

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