5-*exo*-H in II should receive smaller spin density than 6-*exo*-H, and also should show a contact shift of the opposite sign. Much smaller shifts are expected for 5-*endo*-H. The largest observed pmr shifts, excluding those of 8-H and 8-CH_3, in the V(III) complexes of hmc and atc are those of signals u–z and g–l, respectively (see Figures 3 and 4). It has been demonstrated that these signals arise from a single kind of proton, and, on basis of the argument given above, they are assigned to 6-*exo*-H. The other three methylene signals are probably under the envelope of the 1- and 7-methyl resonances.

In summary it can be said that a high degree of stereoselectivity is induced by the ligands in complexes I; the chirality of the predominant diastereomer is determined by the chirality of the ligands. For Co(III) complexes the degree of stereoselectivity is not known. However, for the V(III) complexes it has been shown that stereoselectivity is not complete and that the extent of stereoselectivity may be measured by nmr signal integration in some cases. We are presently engaged in investigating complexes of other dissymmetric ligands with several metal ions in order to assess the effects of increasing or decreasing interligand interactions on the extent of stereoselectivity.

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Kinetics of the Addition of Hydridopentacyanocobaltate(III) to Some α,β-Unsaturated Compounds[1]

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Abstract: The kinetics of the addition of $Co(CN)_5H^{3-}$ to various α,β-unsaturated compounds, $CH_2{=}C(R)X$ (where R = H or CH_3 and X = CN, COOH, COO^-, C_6H_5, $CH{=}CH_2$, α-C_5H_4N, or α-$C_5H_4NH^+$), to yield adducts of the type $Co(CN)_5C(CH_3)(R)X^{n-}$ have been examined. Each reaction was found to exhibit second-order kinetics in accord with the rate law, $k[Co(CN)_5H^{3-}][CH_2{=}C(R)X]$. The values of k, determined in 50 vol. % aqueous methanol, at 25° and 0.5 M ionic strength, ranged from $1.5 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for $CH_2{=}CHCOO^-$ to $4.7 \times 10^2\ M^{-1}\ sec^{-1}$ for $CH_2{=}CHC_5H_4NH^+$. The rates of reaction were found to be independent of the concentration of added CN^- and (except for acrylate and 2-vinylpyridine where protonation of the substrate to the more reactive acid form resulted in an increase in rate below pH 8) of the pH of the solution. The significance and mechanistic implications of the kinetic results are discussed.

In this paper we describe an investigation of the kinetics of the addition of hydridopentacyanocobaltate(III), $Co(CN)_5H^{3-}$ (hereafter referred to as CoH), to various α,β-unsaturated compounds, $CH_2{=}C(R)X$, where R = H or CH_3 and X = CN, COOH, COO^-, C_6H_5, $CH{=}CH_2$, α-C_5H_4N, or α-$C_5H_4NH^+$. These reactions yield, initially at least, adducts of the type $Co(CN)_5C(CH_3)(R)X^{n-}$ (hereafter referred to as $CoC(CH_3)(R)X$) in accord with eq 1.

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN_5)C(CH_3)(R)X^{n-} \quad (1)$$

Ever since they were first described by Kwiatek and his coworkers,[2-5] the study of these reactions has attracted considerable interest. Contributing to this interest is the role played by such reactions in the mechanism of the $Co(CN)_5{}^{3-}$-catalyzed homogeneous hydrogenation of unsaturated compounds,[4,5] as well as the more general widespread current interest in the whole class of insertion reactions to which the present examples belong.[6] While most of the earlier investigations of the addition reactions of CoH have been concerned primarily with their stoichiometry and with characterization of the organocobalt adducts, two recent papers, which appeared while the present investigation was in progress, report some kinetic results. The first of these by Jackman, Hamilton, and Lawlor[7] lists half-lives at a fixed concentration of reactants for the reactions of CoH with acrylate and various other α,β-unsaturated acids. The other paper, by Burnett, Connolly, and Kemball,[8] describes a detailed investigation of the $Co(CN)_5{}^{3-}$-catalyzed hydrogenation of 1,3-butadiene including kinetic measurements on the addition of CoH to butadiene and on the subsequent rearrangements of the adduct. The present paper reports some further kinetic measurements on these reactions as well as on the reactions of CoH with a number of other substrates.

Experimental Section

Materials. Butadiene (Matheson CP Grade) was used without purification. The other unsaturated substrates (sources in paren-

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[1] Support of this work through grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] J. Kwiatek and J. K. Seyler, "Proceedings of the 8th International Congress on Catalysis, Vienna, 1964," Springer-Verlag, Vienna, 1964, p 308.

[3] J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, 3, 421 (1965).

[4] J. Kwiatek, *Catalysis Rev.*, 1, 37 (1967).

[5] J. Kwiatek and J. K. Seyler, Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., 1968, p 207.

[6] R. F. Heck, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 181.

[7] L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Am. Chem. Soc.*, 90, 1914 (1968).

[8] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc., A*, 991 (1968).

Table I. Spectral Characterization of Adducts

		Uv spectrum[a]		
Substrate	Structure of adduct	λ_{max}, mμ	ϵ_{max}	Pmr spectrum[b]
$CH_2{=}CHCOO^-$	$[CoCH(CH_3)COO^-]^{4-}$ [c]	280	$(3 \pm 1) \times 10^3$	. . .
$CH_2{=}CHCN$	$[CoCH(CH_3)CN]^{3-}$ [c]	253	1.4×10^4	CH_3 doublet at δ 1.35 ($J = 7$ cps); CH unresolved multiresonance at δ 2.22
$CH_2{=}CH\text{-}2\text{-}C_5H_4N$	$[CoCH(CH_3)\text{-}2\text{-}C_5H_4N]^{3-}$ [c,d]	340	$(5 \pm 1) \times 10^3$	CH_3 doublet at δ 1.56 ($J = 7$ cps); CH quartet at δ 3.37; heterocyclic protons unresolved bands at δ 7.0–8.2
$CH_2{=}CHC_6H_5$	$[CoCH(CH_3)C_6H_5]^{3-}$	303	$(1.5 \pm 0.5) \times 10^3$	. . .
$CH_2{=}CHCH{=}CH_2$	$[CoCH_2CH{=}CHCH_3]^{3-}$ [c,e]	285	$(6 \pm 1) \times 10^3$	See ref 3
$CH_2{=}C(CH_3)CH{=}CH_2$	$[CoCH_2CH{=}C(CH_3)_2]^{3-}$ [f]	295	$(9 \pm 1) \times 10^3$	$(CH_3)_2$ singlet at δ 1.74; CH_2 doublet at δ 2.47 ($J = 8$ cps); CH unresolved band at δ *ca.* 4.9
$CH_2{=}C(CH_3)CN$	$[CoC(CH_3)_2CN]^{3-}$ [c]	260	$(6 \pm 1 \times 10^3)$	. . .

[a] Except for the adduct of acrylonitrile, for which the spectral measurements are based on solutions of the recovered pure compound, the uv spectral data are based on measurements of the solution, immediately following reaction, assuming a quantitative yield of the product. [b] In D_2O, δ values are downfield relative to DDS. [c] Previously characterized by Kwiatek, *et al.*,[4] and references therein. [d] Previously prepared and characterized by Johnson, *et al.*[9] [e] The uv spectrum reported is based on the product of reaction of CoH and butadiene at high pH and high CN^-. According to Burnett, *et al.*,[8] the initial product under these conditions is the 1,2 adduct $CoCH(CH_3)CH{=}CH_2$, which, however, spontaneously rearranges to the depicted 1,4 adduct $CoCH_2CH{=}CHCH_3$. [f] The pmr spectrum, obtained in the presence of added CN^-, supports the proposed 1,4-adduct structure. The uv spectrum obtained under the same conditions presumably corresponds to the same species. However, by analogy with the corresponding observations for butadiene, it seems likely that the initial reaction product is the 1,2 adduct, $CoC(CH_3)C(CH_3){=}CH_2$, which spontaneously rearranges to the 1,4 adduct.

theses) were redistilled before use: acrylonitrile (Eastman), bp 69°; acrylic acid (Eastman), bp 39–41° (11 mm); methacrylonitrile (Matheson Coleman and Bell), bp 50° (10 mm); styrene (Eastman), bp 33° (10 mm); 2-vinylpyridine (Aldrich), bp 30–31° (10 mm); isoprene (Matheson Coleman and Bell), bp 33–34°. Potassium cyanide, cobaltous chloride, potassium chloride, and sodium chloride were Baker AR grade reagents.

Aqueous solutions of $Co(CN)_5H^{3-}$ were conveniently prepared by subjecting solutions of pentacyanocobaltate(II) (generally containing 0.06 to 0.08 *M* $Co(CN)_5{}^{3-}$ and an equivalent excess of free CN^-) at room temperature to hydrogen at *ca.* 150 psi in a Parr Series 4500 stirred autoclave for 12 hr. The stability of $Co(CN)_5H^{3-}$ is greatly enhanced by the high pressure of hydrogen, and such solutions could be kept unchanged under these conditions for several days. The exact concentration of $Co(CN)_5H^{3-}$ was determined spectrophotometrically, after appropriate dilution, using the 305-mμ absorption band (ϵ_{max} 610).

Kinetic Measurements. In order that all the reactions could be studied in the same medium, 50 vol. % aqueous methanol was used as solvent. The following buffers were used to maintain the pH (measured directly with a Beckman pH meter using a Beckman 39182 combination electrode) at the desired values; pH 1–3, potassium chloride–hydrochloric acid; pH 3–6, sodium acetate–acetic acid; pH 6–8, monopotassium dihydrogen phosphate–sodium hydroxide; pH 9–11, sodium hydrogen carbonate–sodium carbonate; pH 11–13, sodium hydrogen carbonate–sodium carbonate–sodium hydroxide. The ionic strength was generally maintained at 0.5 *M* with potassium chloride (0.2 *M* in the case of acrylonitrile and 0.5 *M* NaCl in the case of styrene, to prevent the development of turbidity in the reaction solution). All kinetic measurements were made at 25.0 ± 0.1°.

The kinetics of the reactions were followed spectrophotometrically, using a Cary 14 spectrophotometer with a thermostated cell compartment. The reaction vessel was a nitrogen-purged, serum-capped 1-cm cylindrical cell into which the components of the reaction mixture were introduced as oxygen-free solutions by means of nitrogen-purged hypodermic syringes. The order of addition was first the buffer solution, followed by injection of the CoH with a microsyringe, and finally the reaction was initiated by rapid injection of an appropriate aliquot containing a known large excess of the organic substrate.

The reaction was generally followed by measuring the increase in absorbance at a wavelength (in the range 260–340 mμ) close to the absorbance maximum of the organocobalt adduct (see Table I). Where appreciable, the absorption due to the organic substrate was compensated by adding an equivalent concentration to the reference solution. The reactions were generally sufficiently rapid that it was practical to follow them to completion. Under the conditions of the kinetic measurements (*i.e.*, with the organic substrate in substantial excess over CoH), the reactions exhibited pseudo-first-order kinetics. Pseudo-first-order rate constants (k') were determined either from first-order plots (ln A_t *vs.* t) or from Guggenheim plots (ln $(A_t - A_{t+\tau})$ *vs.* t, where A_t is the absorbance at time t and τ is a constant time interval, generally $\geqslant$ 3 half-lives); the rate constants yielded by the two methods agreed well with each other.

Isolation and Characterization of Products. The only adduct which was sufficiently stable to be isolated in *pure form* was that of acrylonitrile. The isolation was effected using a procedure adapted from Kwiatek and Seyler.[3] A solution of HCo (85 ml, 6.5×10^{-2} *M*) was added under nitrogen to acrylonitrile (*ca.* 0.1 mole) in a 65% aqueous acetone solution of potassium hydroxide (100 ml, 2×10^{-3} *M*). Instantaneous reaction was marked by appearance of a yellow color. After shaking for a further 20 min, the solution was poured into deaerated acetone (1 l.). Following the settling of a brown oil, the supernatant liquid was decanted and the brown oil triturated with methanol. The resulting yellow solid was filtered (0.75 g) and combined with the additional product (*ca.* 1 g) recovered by addition of ether to the mother liquor at 0°. Recrystallization (twice) from aqueous acetone–methanol–ether gave the compound (0.2 g) $K_3[Co(CN)_5CH(CH_3)CN]$. *Anal.* Calcd for $K_3CoC_8H_4N_6$: K, 32.5; Co, 16.4; C, 26.7; H, 1.12; N, 23.3. Found: K, 32.0; Co, 16.5; C, 24.4; H, 1.85; N, 23.1. A KBr pellet exhibited CN stretching frequencies at 2200 (vs), 2130 (vs, sh), 2105 (vs), and 2070 cm^{-1} (w, sh). The uv and pmr spectra of the compound are described in Table I. The latter spectrum is consistent with the assigned structure of the adduct, $CoCH(CH_3)(CN)^{3-}$. A D_2O solution of this compound was stable in air for many days.

Modification of the above procedure yielded impure samples of the potassium salts of two other adducts, namely those of 2-vinylpyridine (ν_{CN} at 2120 (vs) and 2100 cm^{-1} (s, sh)), and of isoprene (ν_{CN} at 2125 (vs) and 2080 cm^{-1} (vs, sh), $\nu_{C=C}$ at 1650 cm^{-1} (s, very broad), and other bands at 1370 (s, very broad) and 410 cm^{-1} (s)). The compounds were too unstable to withstand the recrystallization procedures required for purification, but served for the preparation of the concentrated solutions used to determine the pmr spectra given in Table I. The 2-vinylpyridine adduct appeared to be fairly stable as a dry solid but decomposed in solution during the pmr measurement.

The other adducts were too unstable for recovery as salts, and characterization of these was confined to determination of their uv spectra in solution. These spectral measurements, summarized in Table I, were made on the reaction solutions immediately following reaction, and the reported extinction coefficients are based on the assumption (supported by the results of the spectral titrations to be described) that the initial reaction is quantitative.

Uv spectra were recorded with a Cary 14 spectrophotometer. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer. Pmr spectra were determined with a Varian A-60 spectrometer.

Microanalyses were performed by Schwarzkopf Laboratories, Woodside, N. Y.

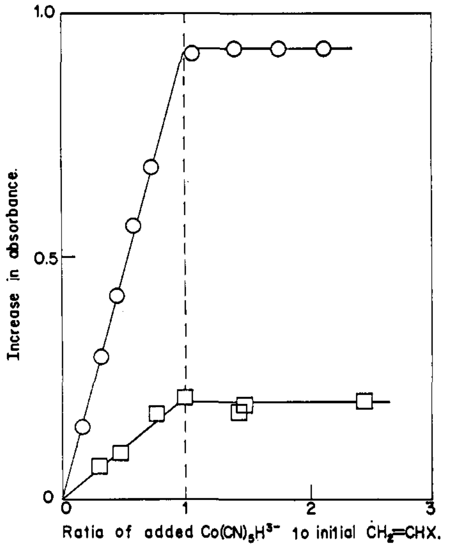

Figure 1. Spectral titrations of 2.8×10^{-3} M vinylpyridine at 430 mμ (○) and of 1.15×10^{-3} M butadiene at 380 mμ (□) with $Co(CN)_5H^{3-}$.

Results and Discussion

Stoichiometry and Products. Most of the reactions which are included in this investigation have been previously described and the organocobalt products previously characterized by a variety of methods (the applicability of which depended on the stability of the adducts) including ir and pmr spectroscopy and chemical characterization.[3,4,9] The stoichiometry of reaction, described by eq 1, and the structural assignments given in Table I are in accord with the earlier assignments and are further supported by (i) the results of spectral titrations such as those depicted in Figure 1, which were performed on several representative substrates (notably 2-vinylpyridine, methacrylonitrile, and 1,3-butadiene) and which confirmed that the stoichiometry of the CoH + $CH_2{=}C(R)X$ reaction in each case was close to 1:1, and (ii) the pmr spectra of the adducts of those substrates (acrylonitrile, 2-vinylpyridine, and isoprene) which were sufficiently stable to withstand the necessary concentration procedures.

In constrast to the other substrates, which yielded 1,2 adducts, *i.e.*, $CoC(CH_3)(R)X$, in accord with eq 1, the pmr spectra of the CoH adducts of butadiene and isoprene support the 1,4 adduct structures shown in Table I, *i.e.*, $CoCH_2CH{=}CHCH_3$ and $CoCH_2CH{=}C(CH_3)_2$, respectively. However, Burnett, Connolly, and Kemball[8] have recently shown that the *initial* product of reaction of CoH with 1,3-butadiene is actually the 1,2 adduct, $CoCH(CH_3)CH{=}CH_2$, which subsequently rearranges (with a rate constant of 4.0×10^{-5} sec^{-1}) to the observed 1,4 adduct (and, at lower CN^- concentrations, also to a π-allyl complex). It seems likely that this is the case also for the reaction of CoH with isoprene and, thus, that the initial reaction in each case is the 1,2 addition of CoH, in accord with eq 1.

Kinetics. All the reactions exhibited second-order kinetics, first order in each of the reactants, in accord with the rate law

$$-d[CoH]/dt = k[CoH][CH_2{=}C(R)X] \qquad (2)$$

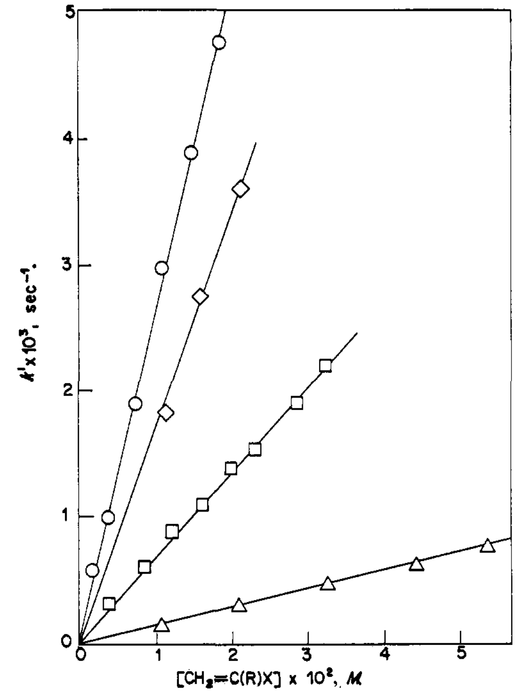

Figure 2. Dependence of the pseudo-first-order rate constant (k') on the concentration of unsaturated substrate: △, acrylonitrile; □, 2-vinylpyridine; ◇, butadiene; ○, isoprene.

Under the conditions of our measurements, *i.e.*, with the organic substrate in large excess over CoH, the observed kinetic behavior was pseudo first order, *i.e.*

$$-d \ln [CoH]/dt = k' \qquad (3)$$

where

$$k' = k[CH_2{=}C(R)X] \qquad (4)$$

Values of the pseudo-first-order rate constants, k', were determined, as described earlier, and plotted against the concentration of $CH_2{=}C(R)X$, yielding in each case linear plots similar to those in Figure 2, from the slopes of which the values of k, listed in Table II, were determined. Our value of k for $CH_2{=}CHCOO^-$ (1.5×10^{-3} M^{-1} sec^{-1}) is in excellent agreement with the value of 1.4×10^{-3} M^{-1} sec^{-1}, computed from the half-life for this reaction, reported by Jackman, *et al.*[7] On the other hand, our value of k for butadiene is only about one-fifth the value of 7.4 M^{-1} sec^{-1} reported by Burnett, *et al.*,[8] *in aqueous solution;* it is possible, although somewhat surprising, that the discrepancy is due to the difference between the two media.

Kinetic measurements for each reaction were made over a range of pH values (generally 3–12) and of CN^- concentrations (generally 1×10^{-4} to 0.5 M). In no case was any dependence on the CN^- concentration detected. Furthermore, no pH dependence was found for any of the reactions except those of acrylate and of 2-vinylpyridine. As shown in Figure 3, the rates of reaction of CoH with these substrates were essentially pH independent above pH 8 but increased at lower pH. The pH dependence in these cases is attributable to protonation of the substrates and could be fitted quantitatively (see Figure 3) to expressions of the form

$$k' = k_A[CH_2{=}CHCOO^-] + k_{AH}[CH_2{=}CHCOOH] \qquad (5)$$

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[9] M. D. Johnson, M. L. Tobe, and L.-Y. Wong, *J. Chem. Soc.*, *A*, 929 (1968).

Table II. Summary of Kinetic Measurements[a]

Substrate	Substrate concn, M	pH range	k,[b] M^{-1} sec^{-1}
$CH_2=CHCOO^-$	0.1-0.7	8-12	$(1.5 \pm 0.5) \times 10^{-3}$
$CH_2=CHCOOH$	0.22	<8[c]	$(2.0 \pm 0.5) \times 10^{-2}$
$CH_2=CHCN$	0.01-0.11	4-12	$(1.8 \pm 0.2) \times 10^{-1}$
$CH_2=CH\text{-}2\text{-}C_5H_4N$	3×10^{-3}-3×10^{-2}	7.7-12	1.0 ± 0.1
$CH_2=CHC_6H_5$	5×10^{-3}-6×10^{-2}	5-12	1.1 ± 0.5
$CH_2=CHCH=CH_2$	0.01-0.5	6.8-10	1.6 ± 0.2
$CH_2=C(CH_3)CH=CH_2$	1×10^{-3}-3×10^{-2}	3-12	2.5 ± 0.2
$CH_2=C(CH_3)CN$	2×10^{-3}-2×10^{-2}	3-12	4.0 ± 1.0
$CH_2=CH\text{-}C_5H_4NH^+$	3.4×10^{-3}	<8[c]	$(4.7 \pm 0.5) \times 10^{2}$

[a] All kinetic measurements in 50 vol. % aqueous methanol at 25°. Ionic strength maintained at 0.5 M with KCl unless otherwise noted. Initial CoH concentration generally in the range 3×10^{-4} to 1×10^{-3} M. [b] Independent of the concentration of CN^- from 1×10^{-4} to 0.5 M. [c] See text.

and

$$k' = k_A[CH_2=CHC_5H_4N] + k_{AH}[CH_2=CHC_5H_4NH^+] \quad (6)$$

using the experimentally determined pK_a values (in the reaction medium) of 5.2 and 4.3 for $CH_2=CHCOOH$ and $CH_2=CHC_5H_4NH^+$, respectively, to determine the concentrations of the protonated and unprotonated forms of the substrate. The values of k for each form, determined in this way, are listed in Table II.

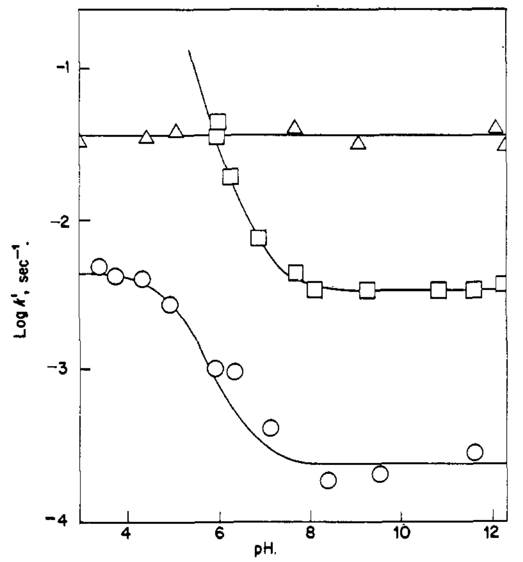
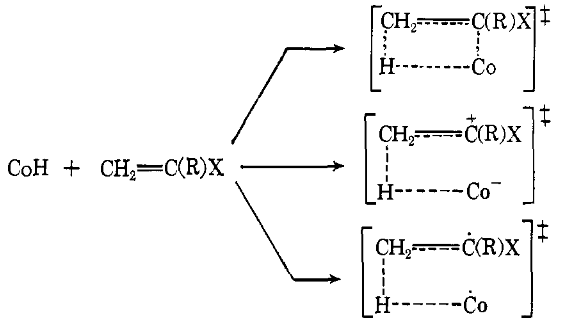


Figure 3. pH dependence of the rates of reaction of $Co(CN)_5H^{3-}$ with various substrates: ○, 0.22 M acrylate; □, 3.4×10^{-3} M 2-vinylpyridine; △, 1.1×10^{-2} M isoprene. The curves for acrylate and 2-vinylpyridine are computed from eq 5 and 6, respectively, using the values of k in Table II.

Kinetic Trends and Mechanistic Implications. The values of k, for the reactions of CoH with the various unsaturated substrates, spanned a 10^5-fold range, from 1.5×10^{-3} M^{-1} sec^{-1} for $CH_2=CHCOO^-$ to 4.7×10^2 M^{-1} sec^{-1} for $CH_2=CHC_5H_4NH^+$. Part of this variation appears to be due to electrostatic effects, reflecting the variation in the charges of the substrates, but even for the neutral substrates the variation in k is still appreciable, ranging from 2.0×10^{-2} M^{-1} sec^{-1} for $CH_2=CHCOOH$ to 4.0 M^{-1} sec^{-1} for $CH_2=C(CH_3)CN$. The principal significant trends appear to be (i) the decrease in reactivity toward CoH on going from 1,3-butadiene or styrene to 2-vinylpyridine, acrylonitrile, or acrylic acid (*i.e.*, on increasing the electron-withdrawing power of the substituent X, in $CH_2=CHX$), and (ii) the increase in reactivity on methylation of the substrate, *i.e.*, on going from $CH_2=CHX$ to $CH_2=C(R)X$. These trends are suggestive of an electrophilic, rather than nucleophilic, attack on the double bond of the substrate.

Several different limiting descriptions, depicted in eq 7, can be envisaged for the mechanisms of the reactions under consideration, in which the initial interactions of CoH with the substrates are characterized by the following features: (i) a concerted addition of CoH to the double bond through a four-center transition state resembling that of eq 7a; (ii) initial proton transfer from CoH to the double bond through a transition state resembling that of eq 7b; (iii) initial H-atom transfer from CoH to the double bond through a transition state resembling that of eq 7c.



(7a)

(7b)

(7c)

The first mechanism has the attractive features that it leads most directly to the formation of the product adduct, $CoC(CH_3)(R)X$, and that it invokes bonding between Co and $-C(R)X$ to stabilize the transition state. It is not clear, however, that a configuration which accommodates such bonding is favorable on steric grounds. Nor does this mechanism provide a convenient explanation for the observed kinetic trends and, in particular, for the observation that $k(CH_2=CRX) > k(CH_2=CHX)$, with which it is difficult to reconcile on steric grounds.

The remaining two alternatives can be regarded as limiting descriptions of a common mechanism in which bonding between Co and $-C(R)X$ makes little, if any, contribution to stabilization of the transition state. Both are consistent with the observed kinetic trends. Mechanism ii is considered less favorable in view of the extremely low basicity of $Co(CN)_5H^{3-}$ (spectrophotometric and kinetic evidence derived from these and other studies indicate that the pK_a of CoH $\gg$ 14). On the other hand, the measured[10] bond dissociation energy of 57 kcal/mole for the CoH bond in $Co(CN)_5H^{3-}$ leads to the conclusion that for most, if not all, of the substrates under consideration the outright transfer of a H atom, according to eq 8, is close to thermoneutral, a conclusion that tends to favor mechanism iii.

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN)_5^{3-} + CH_3\dot{C}(R)X \quad (8)$$

Supporting this conclusion is the kinetic evidence advanced by Simandi and Nagy[11] that the $Co(CN)_5^{3-}$-catalyzed hydrogenation of cinnamate involves the rate-determining H-atom transfer step

$$Co(CN)_5H^{3-} + C_6H_5CH{=}CHCOO^- \longrightarrow Co(CN)_5^{3-} + C_6H_5\dot{C}HCH_2COO^- \quad (9)$$

A similar mechanism has been proposed[12] for the $Co(CN)_5^{3-}$-catalyzed hydrogenation of styrene.

It is significant, and perhaps further indicative of the unimportance of Co···C(R)X bonding in the transition states of these reactions, that the kinetic trends fail to parallel the stabilities of the $CoC(CH_3)(R)X$ adducts which, in contrast to the corresponding rates, are clearly greatest for acrylonitrile and 2-vinylpyridine.

Significance is also attached to the absence of any CN^- dependence of the rates of these reactions. This observation appears to rule out mechanisms involving preequilibria such as

$$Co(CN)_5H^{3-} \rightleftarrows Co(CN)_4H^{2-} + CN^- \quad (10)$$

$$Co(CN)_5H^{3-} + CH{=}C(R)X \rightleftarrows Co(CN)_4(CH_2{=}C(R)X)H^{2-} + CN^- \quad (11)$$

This conclusion is of interest in view of the suggestion frequently encountered[6] that "insertion" of unsaturated molecules into metal–ligand bonds may require prior coordination to the metal, by reaction with a coordinately unsaturated complex.

(10) B. De Vries, *J. Catalysis*, **1**, 489 (1962).
(11) L. Simandi and F. Nagy, *Acta Chim. Hung.*, **46**, 137 (1965).
(12) W. Stroheimer and N. Iglauer, *Z. Physik. Chem.* (Frankfurt), **51**, 50 (1966).

A Molecular Orbital Study of the *trans* Influence and Kinetic *trans* Effect in Square-Planar Platinum(II) Complexes[1]

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Abstract: Extended Hückel molecular orbital calculations were carried out on a series of square-planar platinum(II) complexes of the type *trans*-$PtCl_2(L)(NH_3)$, where L represents a number of different kinds of σ-bonding ligands. These calculations were done to explore the *trans*-influence phenomenon and the kinetic *trans* effect. Calculation of the over lap populations and overlap energies for the above series of molecules gave evidence for a *trans*-influence series very similar to the kinetic *trans*-effect series for σ-bonding ligands. A *cis* influence comparable in magnitude to the *trans* influence was also observed. The molecular orbital calculations were found to support, qualitatively and quantitatively, a mechanism for the kinetic *trans* effect for σ-bonding ligands which is based on stabilization of the activated complex by σ-donor interactions.

The square-planar complexes of Pt(II) have interested chemists for many years. A great many kinetic studies have been conducted on these complexes, and there is much experimental evidence for the phenomenon called the *trans* effect.[2–4] It has been found that ligands can be arranged in a series based upon their ability to labilize the *trans* group in the square-planar complexes of Pt(II). Qualitatively, this labilizing effect decreases in the order[3] $C_2H_4 \sim NO \sim CO \sim CN^- > R_3P \sim H^- \sim SC(NH_2)_2 > CH_3^- > C_6H_5^- > SCN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$.

The above series is based upon the relative rates of substitution of the ligand *trans* to the *trans* director, L, as L is varied. Very few of the kinetic studies on these complexes have included measurements of the enthalpies and entropies of activation for the substitution reactions, and many of these studies have been conducted in very polar solvents. These facts make it more difficult to isolate the reason or reasons for the apparent labilizing effect of the *trans* director.

Since the *trans* effect is defined as the influence of the *trans* director on the rate of substitution of the *trans* ligand, to explain the *trans* effect one should consider the effects of L on the activation energy for the reaction. The *trans* director can lower the activation energy for the substitution reaction by destabilizing the ground state of the complex or by stabilizing the activated complex or both. Most early theories of the *trans* effect[5–8] emphasized destabilization of the ground state by weakening of the bond *trans* to L. More recent explanations have emphasized the effects of L on the

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