experiment, 10 mg of $C_5H_5V(CO)_4$ was dissolved in 10 ml of ligand solution in a foil-wrapped vessel equipped with a rubber septum. Air was rigorously excluded from the reaction by carefully purging the solution and vessel with nitrogen. Samples were withdrawn from the reaction solution with a syringe, preceded by the injection of a small volume of nitrogen; the absorbances of the samples were immediately measured on a Perkin-Elmer 237b infrared spectrophotometer. The initial experiments with the various ligands were also monitored by scanning the carbonyl stretching region on a Beckman IR-8 equipped with an external recorder or a Beckman IR-12 infrared spectrophotometer. The concomitant increase in product bands was observed with the disappearance of the $C_5H_5V(CO)_4$ bands. Pseudo-first-order reaction conditions were maintained by using ligand concentrations of greater than 10-fold excess. Plots of ln $(A_t - A_\infty)$ *vs.* t (where A_t is absorbance at time t and A_∞ is absorbance after completion of reaction; in most cases, A_∞ was taken to be the absorbance of the solvent–ligand blank since the values were essentially identical with those at the completion of the reaction) were linear to at least 75% of reaction. The pseudo-first-order rate constants, k_{obsd}, were determined graphically and are reproducible to within 6% or better (Table II).

TABLE II

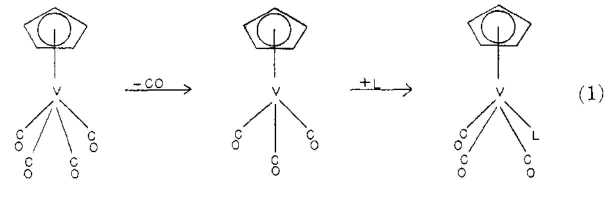
RATES OF REACTION OF $C_5H_5V(CO)_4$ WITH VARIOUS LIGANDS IN DECALIN[a]

Ligand, L	Concn, *M*	Temp, °C	10^4k_{obsd}, sec^{-1}
$P(C_4H_9)_3$	0.062[b]	109.5	0.810
	0.062		0.840
	0.178		0.722
	0.407		0.770
	0.454		0.789
	0.103	119.3	2.48
	0.190		2.68
	0.491		2.62
	0.176[c]		2.45
	0.405[c]		2.45
$P(OC_4H_9)_3$	0.129		2.62
$P(OCH_2)_3C(CH_2)_2CH_3$	0.386		2.51
$P(C_4H_9)_3$	0.198	129.5	8.25
	0.429		8.25
	0.653		8.43

[a] $\Delta H^* = 55.1 \pm 1.2$ kcal/mol; $\Delta S^* = 36.0 \pm 2.8$ eu. [b] Rate determined in the presence of room light. [c] Chlorobenzene solvent.

Results and Conclusions

Kinetic data in Table II indicate that the reaction $C_5H_5V(CO)_4 + L \rightarrow C_5H_5V(CO)_3L + CO$ proceeds according to the first-order rate law: rate $= k[C_5H_5V(CO)_4]$. The rate is thus independent of the ligand L concentration and ligand identity. As indicated in Table II some rate determinations were performed with and without the exclusion of light and in solvents of varying dielectric constant; the rates were very little affected by these alterations. The first-order rate law obtained for the reaction is consistent with a mechanism involving rate-determining dissociation of a carbonyl group (eq 1). The positive entropy of activation (+36 eu) also supports a dissociative mechanism.



(1)

The enthalpy of activation of 55.1 kcal/mol is, to our knowledge, the largest value known for substitution reactions of metal carbonyl complexes. Other $\Delta H^{\ddagger}$ values of approximately 40 kcal/mol have been reported for carbonyl dissociation reactions of $M(CO)_6$[8] (where M = Cr, W) and diphos$M(CO)_4$[9] (where M = Cr, Mo). The fact that the reaction of $C_5H_5V(CO)_4$ proceeds under milder conditions than those of the Cr, Mo, and W complexes previously mentioned is attributable to the large favorable entropy effect accompanying the reaction.

Although second-order kinetics have been reported for the carbonyl substitution and CO-exchange reactions of $C_5H_5Co(CO)_2$[10] and $(C_5H_5)_2Ni_2(CO)_2$,[11] the absence of a second-order term for the $C_5H_5V(CO)_4$ reactions is apparently due to steric influences which inhibit expansion of the metal coordination sphere and/or prevent nucleophilic attack at the carbonyl carbon.

Since the work of Strohmeier and Blumental[1] indicated that the reaction of $C_5H_5V(CO)_4$ with $P(C_6H_5)_3$ was first order in each of the reactants, contrary to our results with other Lewis bases, we attempted to study the reaction under conditions very close to those employed by those investigators. Thus at 102.5° using 0.2 *M* $P(C_6H_5)_3$ in decalin solvent, $C_5H_5V(CO)_4$ was observed to disappear but at a rate which was much slower than reported. Also very little product, $C_5H_5V(CO)_3L$, formed during the reaction; a great deal of decomposition accompanied the small amount of product formation. While the discrepancy between our results and those of Strohmeier and Blumental cannot be accounted for in detail, it is apparently related to the fact that the other authors measured the rates of reaction by following the increase in product absorptions in the visible spectrum; we have found that in fact very little product is formed under their conditions.

Acknowledgment.—We appreciate very much the support of this research by the National Science Foundation (GP-12136).

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Base Adducts of Nickel Ethylxanthate

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We reported several years ago[1] that planar, diamagnetic bis(ethylxanthato)nickel(II), $Ni[S_2CO(C_2H_5)_2]_2$,

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[1] R. L. Carlin, J. S. Dubnoff, and W. T. Huntress, *Proc. Chem. Soc.*, 228 (1964).

which we will call NiX_2, will react with pyridine in benzene to yield only the six-coordinate adduct, $NiX_2 \cdot 2py$. A good isosbestic point was observed, and the thermodynamic functions were reported. We have now refined our measurements, measuring ΔH directly (and more accurately) by calorimetry, and extended our measurements to several other bases as well. We find that several pyridine derivatives without an α substituent likewise form only the bis adduct $NiX_2 \cdot 2B$ but that α substitution leads to steric hindrance at the coordination site, and other equilibria then prevail. Furthermore, it has been shown that triphenylphosphine and several other bulky bases form only a mono adduct.

Experimental Section

Bis(ethylxanthato)nickel(II) was prepared by standard procedures[2] and recrystallized from a 3:2 methanol–chloroform mixture. Nitrobenzene was distilled prior to use, and all the amines were distilled from zinc dust. Triphenylphosphine was recrystallized from a 1:9 benzene–hexane solution. The benzene was Spectranalyzed grade, and all other chemicals were reagent grade.

Equilibrium constants were determined at 25° by spectrophotometric titration in a Cary 14. Solutions in benzene of the metal complex (3×10^{-4} M) were made up with various added concentrations of base and the spectra were recorded promptly. Typical sets of data are collected in the figures. Equilibrium quotients are reported in several cases where the interaction is so small that large concentrations of base are required; the solutions are not ideal, but this does not invalidate the qualitative arguments we offer.

Enthalpies were determined by a published procedure[3] in nitrobenzene at 25°; we have already discussed the reasons for making the thermodynamic measurements in two different solvents.[3] These measurements were restricted to those systems with large equilibrium constants, so that an excess of base was certain to cause the reaction to go to completion.

Results and Discussion

The thermodynamic measurements are collected in Table I, where it is clear that the systems studied can be divided into two classes: (a) those systems that coordinate two donor atoms to NiX_2 in one step, causing the coordination number to rise directly to 6 and (b) those systems that form $NiX_2 \cdot 2B$ but also exhibit evidence for the intermediate five-coordinate adduct, $NiX_2 \cdot B$.

Table I

Reactions of Nickel Ethylxanthate with Bases at 25°

(a) Systems Which go $4 \rightleftharpoons 6$

	K,[a] $l.^2\ mol^{-2}$	$-\Delta H$,[b] kcal mol^{-1}
Pyridine	2150 ± 25	20.33 ± 0.10
3-Picoline	3550 ± 50	19.75 ± 0.41
4-Picoline	7750 ± 650	19.29 ± 0.38
3,5-Lutidine	6100 ± 600	20.44 ± 0.62
α,α'-Dipyridyl	*Ca.* 10^5 l. mol^{-1}	20.11 ± 0.29
Ethylxanthate[c]	*Ca.* 10^5 l. mol^{-1}	. . .

(b) Systems Which go $4 \rightleftharpoons 5 \rightleftharpoons 6$

	K_1,[a] l. mol^{-1}	K_2,[a] l. mol^{-1}
2-Picoline	30	2
2,6-Lutidine	15	1
Quinoline	2	<0.1

[a] Benzene solution. [b] Nitrobenzene solution. [c] Acetone solution.

Case a.—As Figure 1 illustrates, the spectrum of NiX_2 changes regularly as a base such as pyridine is added, and an isosbestic point is observed at about 3800 Å. The change of spectrum with concentration of base allows an evaluation of the equilibrium constant, and the isosbestic point indicates that there are only two absorbing species in the solution. The resulting green solution with a spectrum typical of that of octahedral nickel(II), the isolation of paramagnetic $NiX_2 \cdot 2py$,[2,4] and the constancy of a calculated equilibrium constant as a function of concentration all point to the equilibrium process being the addition of 2 mol of base to form only the six-coordinate adduct

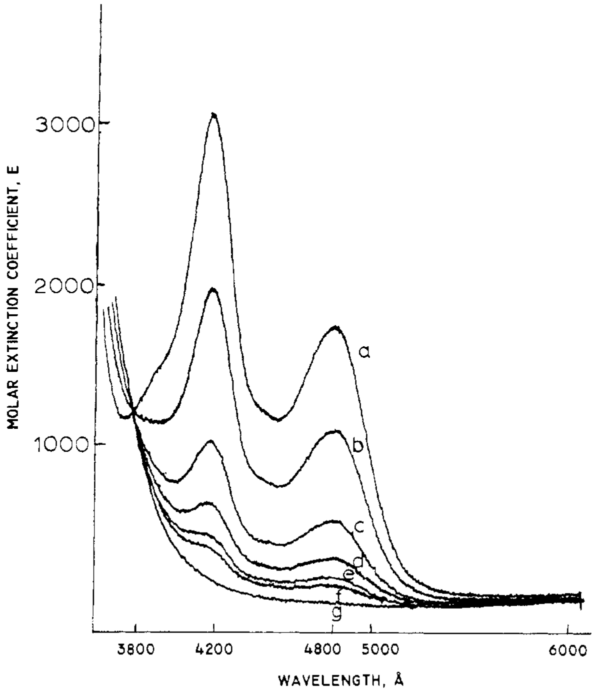

Figure 1.—Spectrophotometric titration of 3×10^{-4} M NiX_2 in benzene with pyridine at successive concentrations of (a) 0, (b) 1.86×10^{-2}, (c) 3.72×10^{-2}, (d) 5.59×10^{-2}, (e) 7.45×10^{-2}, (f) 9.31×10^{-2}, and (g) about 2.5 M.

$$NiX_2 + 2py \overset{K}{\rightleftharpoons} NiX_2 \cdot 2py \quad (1)$$

In view of the stepwise nature of most successive equilibria, it is worth a comment on what we mean by the statement that the five-coordinate adduct does not form. It would be more accurate to say that there is no evidence for the existence of the molecule since we are reporting equilibrium measurements, and the stability of $NiX_2 \cdot 2py$ far outweighs that of $NiX_2 \cdot py$. Kinetic measurements would undoubtedly suggest the intermediation of a five-coordinate adduct. Equilibrium constants were calculated at both 4200 and 4800 Å, and no wavelength dependence was observed.

It is clear from Table I that the class a bases are simply those pyridine bases which do not offer steric hindrance at the donor atom. While our arguments

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(3) R. L. Carlin and F. A. Walker, *J. Am. Chem. Soc.*, **87**, 2128 (1965).

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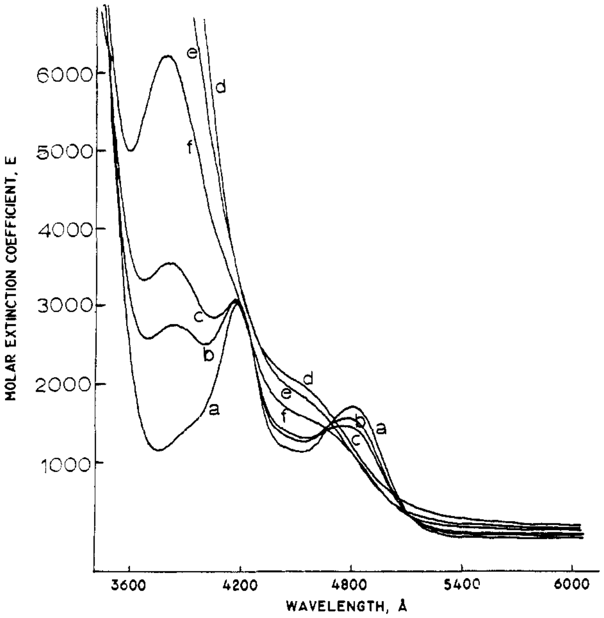

Figure 2.—Spectrophotometric titration of 3×10^{-4} M $\mathrm{NiX_2}$ in benzene with 2-picoline at successive concentrations of (a) 0, (b) 0.51, (c) 1.02, (d) 2.04, (e) 3.06, and (f) 8. 2 M.

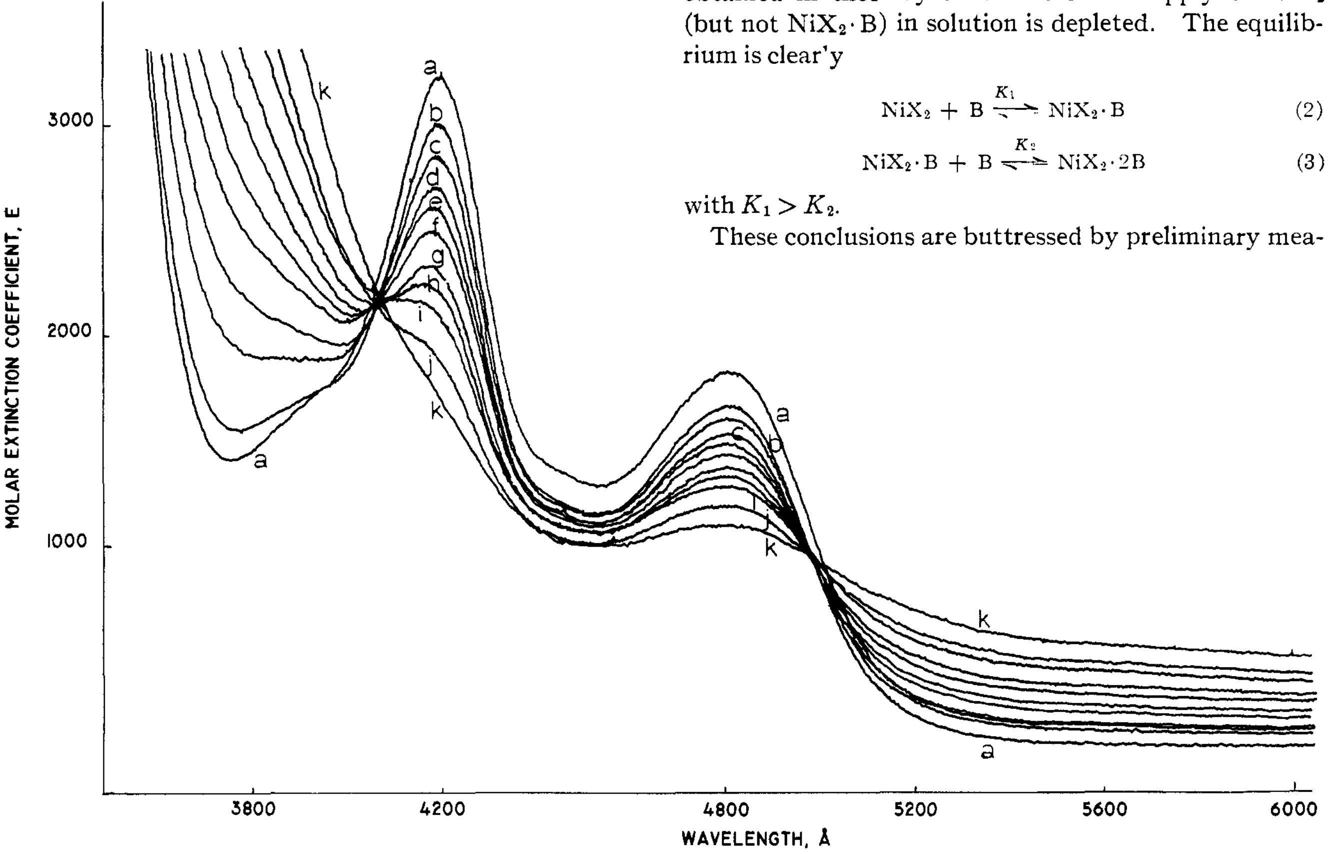

Figure 3.—Spectrophotometric titration of 3×10^{-4} M $\mathrm{NiX_2}$ in benzene with triphenyphosphine at successive concentrations of (a) 0, (b) 1.00×10^{-2}, (c) 3.01×10^{-2}, (d) 5.00×10^{-2}, (e) 7.50×10^{-2}, (f) 10.01×10^{-2}, (g) 15.00×10^{-2}, (h) 20.00×10^{-2}, (i) 30.01×10^{-2}, (j) 50×10^{-2}, and (k) 150×10^{-2} M.

may be based solely on those systems listed in the table, it is likely that our conclusion is more general in nature. Methyl substitution in the 3, 4, or 5 position causes the predicted increase in basicity due to inductive effects *but only as adduced by the equilibrium constants.* The enthalpies of reaction are remarkably insensitive to such methyl substitution and even to the utilization of α,α'-dipyridyl as the interacting base. These data are consistent with earlier conclusions that metal complexes are not very sensitive indicators of base strength.[3,5] The dipyridyl adduct, which exhibits similar spectral behavior, must of course be *cis* octahedral, and its brown color suggests that the green pyridine adducts may be *trans*; this has also been suggested by Jørgensen.[2]

Case b.—As has been implied above and as illustrated by the results in Table I, substitution at the 2 position of pyridine, either by the introduction of methyl groups or of the second ring supplied by quinoline, reduces dramatically the thermodynamic stability of the adducts. This effect is of course anticipated from a great deal of chemical experience. What was unexpected was the appearance of evidence for the five-coordinate adducts with these bases. Thus, an isosbestic point was observed in these systems for low concentrations of base, as illustrated in Figure 2 at 5100 Å, but it is lost as the concentration increases, indicating the formation of (at least) three absorbing species in the solution. A new isosbestic point is then obtained in those systems where the supply of $\mathrm{NiX_2}$ (but not $\mathrm{NiX_2 \cdot B}$) in solution is depleted. The equilibrium is clear'y

$$\mathrm{NiX_2 + B \overset{K_1}{\rightleftharpoons} NiX_2\cdot B} \qquad (2)$$

$$\mathrm{NiX_2\cdot B + B \overset{K_2}{\rightleftharpoons} NiX_2\cdot 2B} \qquad (3)$$

with $K_1 > K_2$.

These conclusions are buttressed by preliminary measurements on such bases as isobutylamine, di-n-butylamine, and tri-n-butylamine. These bulky bases appear to coordinate to $\mathrm{NiX_2}$ to form *only* the mono adducts in dilute solution, but we have not examined these systems thoroughly because of the possibility of

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(5) D. P. Graddon, *Coord. Chem. Rev.*, **4**, 1 (1969).

dithiocarbamate formation.[6] Another example of this class of bases is supplied by triphenylphosphine, for which representative data are shown in Figure 3. A comparison with data in the other figures shows that complete coordination does not occur even at the highest relative concentration of base to metal; in fact, the spectrum of six-coordinate nickel is never obtained in these brown solutions. On the assumption that equilibrium process 2 is the principal one that occurs in this system, an equilibrium quotient of 14 ± 4 M^{-1} is obtained.

Conclusion

While our conclusion that steric hindrance is the main determinant of the nature of the reactions of NiX_2 with α-substituted pyridine-type bases is probably justified, the nature of the steric effect is not at all clear. If the six-coordinate adducts are *trans* octahedral in solution, addition of the first molecule of base may distort the coordination polyhedron so that attack by the second molecule of base is unfavored; if the six-coordinate adducts are either *cis* octahedral or prismatic, then it is possible that the two base molecules simply interfere with one another, as well as with the rest of the acceptor molecule. Perhaps crystal structure analyses of several of the adducts would answer some of these questions, but we have been unable to obtain single crystals of any of the five-coordinate adducts. In any case, arguments based on structures in the solid state become tenuous when applied to equilibrium behavior in solution.

Acknowledgment.—Preliminary results were obtained by R. Lussier and S. Solomons at Brown University. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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The Reduction of Cobalt(III) by Hydrazoic Acid[1]

BY R. C. THOMPSON[2] AND J. C. SULLIVAN[3]

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Two different empirical forms of the rate law for the oxidation of HN_3 by Co(III) in perchlorate media have been reported. The first[4] is written

$$-d[\mathrm{Co(III)}]/dt = [\mathrm{HN_3}][\mathrm{Co(III)}](a + k/[\mathrm{H^+}]) \qquad (1)$$

while the second is[5]

$$-d[\mathrm{Co(III)}]/dt = k[\mathrm{HN_3}]^2[\mathrm{Co(III)}] \qquad (2)$$

The experimental constraints employed in the two studies were not identical. The differences, however, were not drastic enough to reasonably expect the abrupt change in kinetic paths indicated by (1) and (2). A further study of the system has been undertaken in an effort to resolve these apparent anomalies.

Experimental Section

Reagents.—Stock solutions of cobalt(III) in perchloric acid were prepared electrolytically[6] or by acidification of a solution of the cobalt(III) carbonate complex.[7] Two different sources of sodium azide were purified by the method of Browne[8] and standardized by the cerate procedure.[9] Sodium and lithium perchlorate solutions were prepared from the triply recrystallized salts formed by the neutralization of the respective carbonates with perchloric acid. Both Mallinckrodt and G. Frederick Smith perchloric acid and two independent sources of distilled water[6,10] were used.

Procedures.—A Zeiss PMQ-11 spectrophotometer equipped with a thermostated, rapid-mixing sample compartment (mixing time <1 sec) was used to monitor the reaction. Measurements were made either at 6020 Å where cobalt(III) is the principally absorbing species (ϵ 34.5 ± 0.1 M^{-1} cm^{-1}) or at 2800 Å where ϵ(cobalt(III)) is 281 ± 2 M^{-1} cm^{-1} and $\epsilon(HN_3)$ is 25.1 ± 0.1 M^{-1} cm^{-1}. The values for the molar absorptivities are not sensitive to the temperature and (H^+) variations over the range covered in this work. A solution containing the desired amounts of perchloric acid and perchlorate salt was allowed to reach temperature equilibrium (±0.1°) in a 2-cm absorption cell in the sample compartment. An aliquot of either sodium azide or cobalt(III) solution was added, and the reaction was initiated by rapid injection of the other reactant. The output of the photomultiplier detector tube was recorded on a strip chart recorder with chart speed of 240 cm/min. Spectrophotometric observations in appropriate blank experiments demonstrated no significant volatilization of HN_3 nor decomposition of cobalt(III) through the oxidation of water occurred during the reaction time. The $[H^+]$ of the spent reaction mixture was determined by titration with standard base.

The first observation was made within 2 sec after mixing and the reaction was followed to >98% reaction. Cobalt(III) concentrations were calculated from the spectral data (corrections for HN_3 absorbance at 2800 Å runs were applied), and the HN_3 concentrations were calculated from these data and the initial concentrations according to the demonstrated stoichiometry[4]

$$\mathrm{Co^{3+} + HN_3 = Co^{2+} + {}^{3}/_{2}N_2 + H^+} \qquad (3)$$

Values reported for k' were obtained by a least-squares adjustment of the data (15–35 OD, t data points per experiment) in terms of the functional form

$$t = \frac{1}{k'}\left(\frac{1}{[\mathrm{Co^{3+}}]_0 - [\mathrm{HN_3}]_0}\right) \ln \frac{[\mathrm{Co^{3+}}]}{[\mathrm{HN_3}]} + I \qquad (4)$$

Results and Discussion

All the kinetic data were adequately correlated by eq 4. The precision indices assigned to the rate parameter k' were from 0.1 to 1%. The reproducibility of replicate experiments varied between 0.1 and 4%.

A summary of the data obtained at a constant perchloric acid concentration of 3.70 M[11] is presented in

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(1) A portion of this investigation was performed under the auspices of the U. S. Atomic Energy Commission.

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(3) Chemistry Division, Argonne National Laboratory, Argonne, Ill. 60439.

(4) R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *Inorg. Chem.*, **7**, 1876 (1968).

(5) C. F. Wells and D. Mays, *J. Chem. Soc., A*, 2175 (1969).

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(11) This acid concentration was used to facilitate comparison with the results reported in Figures 1 and 2 of ref 5.