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]

*Received January 28, 1970*

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 ε($HN_3$) 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]

$$\mathrm{Co^{3+} + HN_3 = Co^{2+} + {}^3/_2N_2 + H^+} \qquad (3)$$

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

TABLE I

TEST OF RATE EXPRESSION AT $[HClO_4] = 3.70\ M^a$

| 10° | | | 17° | | | 24.8° | | |
|---|---|---|---|---|---|---|---|---|
| Entry | $k'$,[b] $M^{-1}$ sec$^{-1}$ | $[HN_3]_0$, $M$ | Entry | $k'$,[b] $M^{-1}$ sec$^{-1}$ | $[HN_3]_0$, $M$ | Entry | $k'$,[b] $M^{-1}$ sec$^{-1}$ | $[HN_3]_0$, $M$ |
| 1 | $0.894 \pm 0.024$ | $1.58 \times 10^{-2}$ | 4 | $3.02 \pm 0.04$ | $8.05 \times 10^{-3}$ | 8 | $9.56 \pm 0.01$ | $2.71 \times 10^{-3}$ |
| 2[c] | $0.902 \pm 0.012$ | $3.32 \times 10^{-2}$ | 5 | $3.06 \pm 0.02$ | $1.07 \times 10^{-2}$ | 9 | $9.40 \pm 0.15$ | $5.42 \times 10^{-3}$ |
| 3[c] | $0.884 \pm 0.006$ | $1.69 \times 10^{-2}$ | 6[d] | $3.00 \pm 0.01$ | $1.07 \times 10^{-2}$ | 10 | $9.78 \pm 0.08$ | $8.08 \times 10^{-3}$ |
| | | | 7[e] | $3.03 \pm 0.12$ | $5.28 \times 10^{-3}$ | 11 | $9.74 \pm 0.02$ | $1.07 \times 10^{-2}$ |
| | | | | | | 12[f] | $9.62 \pm 0.36$ | $5.52 \times 10^{-3}$ |

[a] $[Co(III)]_0 = (0.70–1.23) \times 10^{-3}\ M$; prepared electrolytically unless otherwise noted. Entry 10 monitored at 6020 Å; otherwise at 2800 Å. [b] Each entry is the average of two or three independent observations. Uncertainties are average deviations. [c] Different source of $NaN_3$. [d] Different source of water and perchloric acid. [e] Co(III) prepared from *ca.* 0.01 $M$ cobalt carbonate complex solution. [f] Order of mixing reversed; Co(III) allowed to stand for 45 min after dilution.

Table I. All of the results are consistent with eq 1, *i.e.*, the reaction is first order in hydrazoic acid and first order in Co(III) concentrations. Entries 2, 3, 6, and 12 indicate that neither the source of sodium azide, water, or perchloric acid nor the order of mixing of the reactants changes the rate parameter outside of the indicated experimental uncertainties. In addition, entry 10 indicates that the value for this parameter (within the same limits) is the same at 2800 or 6020 Å.

The variation of the rate parameter as a function of $H^+$ concentration and variation in ionic strength is presented in Table II. A least-squares adjustment of entries a–e in terms of the functional form

$$k' = a + k/[H^+] \tag{5}$$

yields values of $a = 2.27 \pm 0.05\ M^{-1}$ sec$^{-1}$ and $k = 31.7 \pm 0.1$ sec$^{-1}$. A comparison of these results with those previously reported[4] at an ionic strength of 2.0 maintained with lithium perchlorate of $a = 0.99 \pm 0.66\ M^{-1}$ sec$^{-1}$ and $k = 32.9 \pm 1.2$ sec$^{-1}$ indicates that the "$a$" parameter is apparently most affected by this change in solution composition. Entry f indicates that the value of the rate parameter is not drastically changed when lithium ions are substituted for sodium ions at constant total ionic strength of 5. Entry g is to be compared to the value of $k' = 17.5 \pm 0.2\ M^{-1}$ sec$^{-1}$ reported previously[4] where the measurements were made at 4020 Å with initial concentrations $7.5 \times 10^{-3}$ $M$ Co(III) and $4.9 \times 10^{-3}$ $M$ $HN_3$.

TABLE II

$[H^+]$ AND $I$ DEPENDENCE OF $k'$ AT 24.8°[a]

| Entry | $k'$,[b] $M^{-1}$ sec$^{-1}$ | $[H^+]$, $M$ | $I$, $M$ |
|---|---|---|---|
| a | $8.64 \pm 0.03$ | 5.01 | 5.01 ($NaClO_4$) |
| b | $10.2 \pm 0.1$ | 3.98 | 5.01 ($NaClO_4$) |
| c | $12.7 \pm 0.1$ | 3.02 | 5.01 ($NaClO_4$) |
| d | $17.8 \pm 0.1$ | 2.03 | 5.01 ($NaClO_4$) |
| e | $32.8 \pm 0.1$ | 1.04 | 5.01 ($NaClO_4$) |
| f | $14.1 \pm 0.1$ | 2.99 | 5.01 ($LiClO_4$) |
| g | $16.9 \pm 0.1$ | 2.02 | 2.02 |

[a] $[HN_3]_0 = 5.42 \times 10^{-3}\ M$; $[Co(III)]_0 = 7.66 \times 10^{-4}\ M$. Measurements at 2800 Å. [b] Each entry is the average of two or three independent observations. Uncertainties are average deviations.

The apparent energy of activation calculated from the data in Table I is $27.1 \pm 0.2$ kcal/mol. This value (in 3.70 $M$ $HClO_4$) is to be compared to the value of $25.4 \pm 0.3$ kcal/mol reported[4] at an ionic strength of 2.0 (maintained with $LiClO_4$) for the path inverse in $H^+$. These results are not consistent with the value of 12.6 kcal/mol reported by Wells and Mays.[5]

To learn whether the techniques and spectrophotometric equipment used introduce any variation in the empirical form of the rate law presented in eq 1, Pladziewicz and Webb[12] carried out a limited number of experiments using a Durrum–Gibson stopped-flow spectrophotometer.[13] At 26.6°, 605 nm, 3.90 $M$ $HClO_4$, and an initial Co(III) concentration of *ca.* $4.5 \times 10^{-4}$ $M$ values computed for the second-order rate constant $k$ ($M^{-1}$ sec$^{-1}$) were 12.3, 12.2, and 12.4 for initial concentrations of $HN_3$ 0.013, 0.020, and 0.060 $M$, respectively. All conditions were the same as above except 1.28 $M$ $HClO_4$ ($I = 3.9$ maintained with $NaClO_4$) and 0.020 $M$ initial $HN_3$ concentration; the value for the rate parameter was 31.0 $M^{-1}$ sec$^{-1}$.

The average value of the second-order rate parameter (3.90 $M$ $HClO_4$) computed from the above data for a temperature of 25.0° (using the value of 27.1 kcal/mol for the energy of activation) is 9.56 $M^{-1}$ sec$^{-1}$. This value is to be compared to values of 9.69, 9.63, and 9.59 $M^{-1}$ sec$^{-1}$ obtained at 25° with 3.9 $M$ $HClO_4$, $5.60 \times 10^{-3}$ $M$ $HN_3$, and $6.30 \times 10^{-3}$ $M$ Co(III); the reaction was monitored at 4020 Å using a Cary spectrophotometer.[14]

A number of conflicting reports concerning the degree of polymerization of Co(III) in aqueous perchlorate solutions have been presented.[15] The following observations represent an attempt to determine if variations in the preparation of the Co(III) solutions might cause a kinetically observable effect which could be rationalized in terms of the existence of such species.

The majority of the experiments reported were performed by introducing an aliquot of *ca.* 0.1 $M$ Co(III) in 4 $M$ $HClO_4$ into the reaction mixture. Experiments at 25°, $[HClO_4] = 2.55\ M$, $[Co(III)]_0 = 7 \times 10^{-4}\ M$, and $[HN_3]_0 = 1.0 \times 10^{-2}\ M$ with a freshly prepared stock solution of Co(III) (0.14 $M$, 4 $M$ $HClO_4$) yielded a value of $k' = 13.9 \pm 0.2\ M^{-1}$ sec$^{-1}$; $k' = 13.8 \pm 0.1$ $M^{-1}$ sec$^{-1}$ was determined with a stock solution of Co(III) (0.1 $M$, 4 $M$ $HClO_4$) that had been prepared 6

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(12) J. R. Pladziewicz and T. R. Webb, Department of Chemistry, Iowa State University, Ames, Iowa, personal communication. It is important to note that the reagents used by these investigators represent another independent source of starting materials.

(13) For a description of the equipment and procedures used see: O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 1968 (1969).

(14) These experiments were performed in March 1967 but were not included in the data presented in ref 4.

(15) See the discussion presented by G. R. Davies and B. Warnqvist, *Coord. Chem. Rev.*, in press.

weeks earlier. Entry 12 in Table I indicates that dilution of the stock solution and an "equilibration" period of 45 min yields the same results as obtained without such an elapsed time. Entries 6 and 7 in the same table demonstrate that identical results are obtained when an aliquot of the concentrated Co(III) stock solution is introduced into the reaction mixture as when an aliquot of a sodium azide solution is injected into a dilute (*ca.* $7 \times 10^{-4}$ *M*) Co(III) solution prepared from cobalt(III) carbonate.

All the results presented are correlated by the empirical form of the rate law presented in eq 1. Most of the results were obtained under experimental constraints of temperature, acidity, ionic strength, and initial concentrations of thereactants (Co(III) and $HN_3$) similar to those reported by Wells and Mays.[5] The empirical form of the rate law proposed by these authors, eq 2, however, is not consistent with the data that have been presented.

**Acknowledgment.**—Professor James H. Espenson brought the anomalous rate laws in the literature to the attention of Pladziewicz and Webb and kindly provided them the necessary laboratory facilities.

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## Synthesis and Spectra of Sulfhydryltrimethylplatinum(IV)

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*Received February 5, 1970*

Structural conclusions have been made for tetrameric hydroxytrimethylplatinum(IV) on the basis of nmr and infrared spectra.[2,3] Neutron[4] and X-ray[5,6] diffraction have recently confirmed the tetrameric structure in the solid state. A most interesting feature of the nmr spectrum of this compound is the splitting pattern of the OH proton signal. Each oxygen is bound to three platinum atoms (33.8% $^{195}Pt$, $I = {}^1/_2$) resulting in a seven-line pattern ($J_{Pt-O-H} = 11.2$ Hz, $\tau$ 11.53).

It was thought interesting to synthesize and examine the spectra of the sulfur analog.

### Experimental Section

Sulfatobis(trimethylplatinum(IV)) tetrahydrate was prepared by the method of Pope and Peachey.[7] Sulfatobis(trimethylplatinum(IV)) is water soluble and insoluble in organic solvents, while it was presumed the sulfhydryl derivative would be water insoluble and soluble in organic solvents (similarly to the halo, thiocyanato,[8] and hydroxy derivatives). Benzene was added to an aqueous solution of the sulfato compound and a stream of gaseous hydrogen sulfide passed through the vigorously stirred mixture for 24 hr. The sulfhydryl derivative was extracted into the organic phase which was separated and evaporated to yield a small quantity of brown powder. A yellow crystalline material resulted upon recrystallization from benzene. *Anal.* Calcd for $C_3H_{10}PtS$: C, 13.18; H, 3.69; Pt, 71.38; S, 11.73. Found: C, 13.36; H, 3.64; Pt, 71.20; S, 11.84. Because of the extremely low solubility (and anticipated high molecular weight) an accurate molecular weight determination could not be made.

Sulfhydryltrimethylplatinum(IV) was also prepared by the hydrolysis of the thioacetamide adduct of iodotrimethylplatinum(IV) and the direct reaction of hydroxytrimethylplatinum(IV) with $H_2S$; but in both of these reactions the product was contaminated with starting materials.

Infrared spectra were recorded as Nujol and fluorocarbon mulls on a Perkin-Elmer Model 621 spectrophotometer. Cesium bromide plates were used for the region above 300 $cm^{-1}$ and polyethylene film was used in the region 200–300 $cm^{-1}$.

Nmr data were obtained for benzene solutions using a Varian HA-100 spectrometer. Chemical shifts were referred to the solvent and converted to $\tau$ units having $\tau(C_6H_6)$ 2.74.

### Results and Discussion

The nmr spectrum of $((CH_3)_3PtSH)_4$ is quite similar to that of $((CH_3)_3PtOH)_4$. The methyl proton resonance occurs at $\tau$ 8.52 with $J_{^{195}Pt-C-H_3} = 73.4$ Hz. Corresponding values for $((CH_3)_3PtOH)_4$ are $\tau$ 9.04 and 78.6 Hz. The SH proton signal occurs at $\tau$ 13.29 with $J_{^{195}Pt-S-H} = 15.2$ Hz. Corresponding values for $((CH_3)_3PtOH)_4$ are $\tau$ 11.53 with $J_{^{195}Pt-O-H} = 11.2$ Hz. Due to the low solubility of $((CH_3)_3PtSH)_4$ only the three strongest lines of the SH multiplet could be observed (comprising 85.7% of the theoretical total intensity[2]). We can formulate no reasonable alternative explanation for these data, however, without invoking unexpected five-coordinate platinum species. The most logical explanation is that the structure of $((CH_3)_3PtSH)_4$ is analogous to $((CH_3)_3PtOH)_4$.

The result of increasing the size of the bridging atom is an increase in the bonding interaction with the bridging ligand. This is reflected in the increased "s" character in the Pt–S–H region compared to the Pt–O–H region. The increased chemical shift ("shielding") of the SH proton supports this conclusion as does the *decreased* chemical shift of the methyl protons and the *decreased* value of $J_{^{195}Pt-C-H_3}$ on going from $((CH_3)_3PtOH)_4$ to $((CH_3)_3PtSH)_4$.

$((CH_3)_3PtOH)_4$ has elongated Pt–O bonds of 2.20 Å[4] compared with 1.96 Å from the sum of covalent radii. The increase in bond length implies a rehybridization in the tetramer to provide optimum overlap at the increased distance. The introduction of more directional (pd) character decreases the "s" character of the platinum–bridging atom bond and correspondingly increases it in the Pt–C bond. It would be expected that the effect of increasing the size of the bridging atom would be a lessening of this perturbation which, in turn, should affect the values of the chemical shifts and coupling constants. The values for the chemical shifts of the

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