the band at 14.6 eV arises from the $4a_1'$ MO ionization, and the peak at 17.4 eV is attributed to K 3p ionization exclusively.

The difference of approximately 4.9 eV between the binding energies we report and those measured by Morrison and Hendrickson[7] for NaCN and KNO_3 represents the work function of the sample Ψ_s ($E_B^{vac} - E_B^{Fermi}$).

4. Conclusions

We have demonstrated that it is possible to record the UP spectra of some simple ionic solids and thereby to obtain significant information on their molecular electronic structure. The advantages of UPS over XPS in studies of the valence-electron photoionization of solids have been clearly exemplified. While there are still some technical problems, not dealt with here, which require solution before this technique is generally applicable to solids, it must be apparent that in its present form there is much to be gained from a study of the UP spectra of inorganic (and organic) compounds in the solid phase.

Registry No. NaCN, 143-33-9; KNO_2, 7758-09-0; KNO_3, 7757-79-1; CN^-, 57-12-5; NO_2^-, 14797-65-0; NO_3^-, 14797-55-8.

References and Notes

(1) Sodium cyanide (mp 564 °C; bp 1469 °C) gives a vapor which contains both monomeric and dimeric molecules at ca. 730 °C (R. F. Porter, *J. Chem. Phys.*, **35**, 318 (1961)). Both potassium nitrate (mp 334 °C) and potassium nitrite (mp 440 °C) melt without decomposition. At temperatures above 560 °C (KNO$_3$; E. A. Bordyushkova, P. I. Protsenko, and L. N. Venerovskaya, *Zh. Prikl. Khim.* (*Leningrad*), **40**, 1438 (1967))

or 530 °C (KNO$_2$; P. I. Protsenko and E. A. Bordyushkova, *Zh. Neorg. Khim.*, **10**, 1215 (1965)) the melts begin to release nitrogen, oxygen, and oxides of nitrogen (mainly NO and NO_2). This decomposition is essentially complete at temperatures above 900 °C ("Gmelins Handbuch der anorganischen Chemie", Potassium, System No. 22). For the experiments reported here we developed the following procedure. The sample was degassed by heating at ca. 160 °C for 12–18 h at a pressure of 10^{-8}–10^{-9} Torr. At the end of this time, the gold plate covering the sample stage was cleaned by ion bombardment until the valence-band structure of gold was well defined (resolved), thereby ensuring that contamination was minimized. The temperature of the sample was then raised to just below the melting point of the solid, when the pressure in the chamber began to rise very slowly. The temperature of the boat was then increased to be slightly (10–50 °C) above the melting point of the solid and the pressure in the chamber was allowed to rise to about 10^{-7} Torr for 30 s at this temperature. Heating was then immediately discontinued. The mass spectrum of the vapor produced in this way showed m/e peaks consistent with the presence of the molecular ion in the vapor (m/e 101, KNO$_3$; m/e 85, KNO$_2$), as well as peaks due to potassium (m/e 39, 41), nitrogen (m/e 28), oxygen (m/e 32), and oxides of nitrogen (m/e 30, 46). The vapor produced by heating the solid was allowed to condense on the clean gold plate, which was not cooled to avoid occlusion of gaseous products within the solid. The UV photoelectron spectrum of the solid was measured. At the end of the experiment the condensate could be isolated by washing it from the stage; qualitative analysis showed that it contained sodium and cyanide or both potassium and either nitrate or nitrite, as appropriate. Separate experiments showed that the thermal decomposition of KNO$_3$ and of KNO$_2$ could be easily detected: rapid heating of the sample ca. 800 °C resulted in a sudden increase in pressure (to 10^{-6} Torr) in the chamber (release of N_2, NO, O_2, and NO_2) without any detectable deposition of the potassium salt on the gold plate.

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Kinetics of Oxidation of Hydrazinium Ion by Platinum(IV)

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The kinetics of oxidation of hydrazinium ion by platinum(IV) has been studied spectrophotometrically in sodium acetate–acetic acid buffer. Hydrogen ion has no effect on the rate. Sodium perchlorate accelerates whereas sodium chloride inhibits the rate of oxidation. The empirical rate equation for the reaction is $-d[PtCl_6^{2-}]/dt = k_1k_2[PtCl_6^{2-}][N_2H_5^+]/(k_{-1}[Cl^-] + k_2[N_2H_5^+])$. The evidence for intermediate formation of platinum(III) has been demonstrated. The reaction seems to proceed via the formation of intermediate protonated hydrazyl radical followed by the decomposition of the latter to give N_2 and NH_4^+.

The reactions of hydrazine with several oxidizing agents like manganese(VII),[1] vanadium(V),[2] cobalt(III),[3] manganese-(III),[4,5] iron(III),[5,6] copper(II),[7] perdisulfate,[8] thallium(III),[9] and chromium(VI)[10] have been studied. However, the mechanism of the oxidation of hydrazine by platinum(IV) is yet to be understood. The present investigation reports the results of the oxidation of hydrazinium ion by platinum(IV) under various experimental conditions and a possible reaction mechanism has been proposed.

Experimental Section

Reagents. Hydrazine hydrochloride and other inorganic materials were of AnalaR (BDH) grades. Hydrazine solutions were standardized with potassium iodate under the usual Andrews conditions.[11] A stock

solution of hexachloroplatinate was prepared by dissolving platinic acid (Johnson-Mathey) in dilute hydrochloric acid and was standardized iodometrically. Sodium perchlorate was prepared by the neutralization of perchloric acid with sodium hydroxide. All solutions were made in doubly distilled water. Dioxane was purified by distilling twice with metallic sodium, each time collecting the middle fraction.

Absorption Spectra of Platinum(IV) Solution. The absorption spectra of platinum(IV) solution in the ultraviolet region and in the concentration range $(1.84–5.75) \times 10^{-5}$ M were recorded. No spectral shift was noticed with changes in the concentration of platinum(IV) and the spectrum exhibits a single maximum at 261 nm. Beer's law is found to be valid in this concentration range $(1.84–9.2) \times 10^{-5}$ M.

Kinetic Measurements. The rate of decrease of platinum(IV) concentration was followed from the measurements of absorbancies at 261 nm (where platinum(IV) has its maximum absorbance) in a
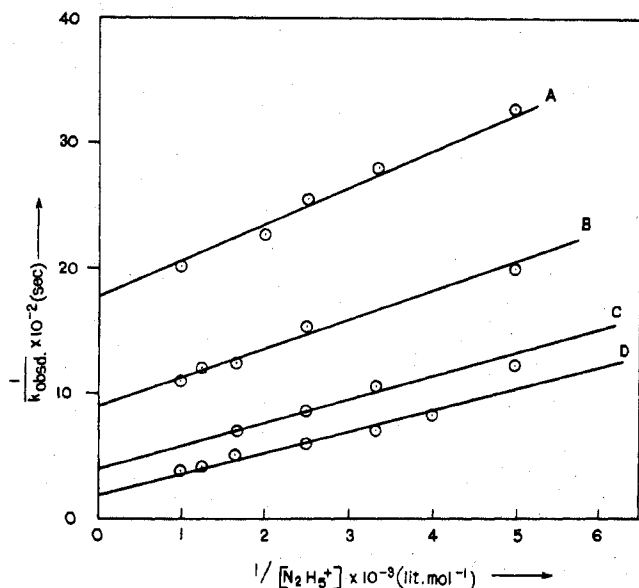
Figure 1. Plots of $1/k_{obsd}$ against $1/[N_2H_5^+]$ at different temperatures; [Pt(IV)] = 2.76 × 10^{-5} M, pH 4.7: A, 15 °C; B, 20 °C; C, 25 °C; D, 30 °C.

Table I. Effect of Sodium Perchlorate Concentrations on the Observed Pseudo-First-Order Rate Constant ([Pt(IV)] = 2.76 × 10^{-5} M, $[N_2H_5^+]$ = 1.0 × 10^{-3} M, pH 4.7)

$10^2[NaClO_4]$, M	0	5.0	10.0	15.0	20.0	25.0
$10^3 k_{obsd}$, s^{-1}	2.85	3.7	4.5	4.9	5.3	6.2

Table II. Effect of Varying Dielectric Constants on the Observed Pseudo-First-Order Rate Constant ([Pt(IV)] = 2.76 × 10^{-5} M, $[N_2H_5^+]$ = 2.0 × 10^{-3} M, pH 4.7)

% dioxane (v/v)	0	5	10	15	20	25
ϵ	76.7	72.2	67.7	63.1	58.6	54.0
$10^3 k_{obsd}$, s^{-1}	5.8	4.9	4.0	3.1	1.42	0.72

Beckman DU Model spectrophotometer. Neither platinum(II) nor other products of oxidation absorb in this wavelength. The cell compartment of the spectrophotometer was kept at constant temperature by circulating water from the thermostat into the surrounding water jackets. Temperature was kept constant within ±0.5 °C. The reaction was studied under pseudo-first-order conditions, i.e., in the presence of a large excess of hydrazine. A 0.2 M NaOAc–0.2 M HOAc buffer was employed throughout. The reaction mixtures with the oxidant in one vessel and the mixture of hydrazinium ion and buffer (and salt or solvent, if any) in the other vessel were separately equilibrated to bath temperature, mixed externally, and then immediately transferred into a cell of path length 1 cm. The rate of decrease of platinum(IV) concentration was followed for at least 80% conversion of the initial platinum(IV) concentration. Generally five to seven experimental points were noted to investigate the reaction. Pseudo-first-order rate constants (k_{obsd}) were obtained graphically from log (absorbance) against "time" plots. The rate constants were reproducible to within ±5%. The reproducibility of the kinetic data was sometimes better than ±5%. The experiments were carried out at 30 °C unless otherwise mentioned. All kinetic investigations were conducted in the presence of air, which was shown to have no detectable effect on the rate constant.

Results

Stoichiometry. Hydrazinium and platinum(IV) solutions of concentrations 1.0 × 10^{-2} and 9.2 × 10^{-4} M were mixed in equal volumes in a sodium acetate–acetic acid buffer of pH 4.7 and kept for 2 h. The unreacted hydrazine was estimated by direct titration with a standard 0.01 M solution of potassium iodate. The $N_2H_5^+$:Pt^{4+} stoichiometry was found to be 1.95. The reaction may be represented according to the equation

$$Pt^{4+} + 2N_2H_5^+ \rightarrow Pt^{2+} + 2NH_4^+ + N_2 + 2H^+ \tag{1}$$

The presence of ammonium ion in solution was tested by the addition of Nessler's reagent.

Effect of Reactant Concentrations. The reaction was studied at different [Pt(IV)] but at constant $[N_2H_5^+]$, pH, and temperature of 1.0 × 10^{-4} M, 4.7, and 15 °C, respectively. The observed pseudo-first-order rate constants were found to be 2.4 × 10^{-4}, 2.45 × 10^{-4}, 2.5 × 10^{-4}, 2.45 × 10^{-4}, and 2.40 × 10^{-4} sec^{-1} at [Pt(IV)] of 2.0 × 10^{-5}, 3.0 × 10^{-5}, 3.68 × 10^{-5}, 5.0 × 10^{-5}, and 6.5 × 10^{-5} M, respectively. This indicates that the order with respect to platinum(IV) is unity. The effect of substrate concentrations was studied by varying the initial substrate concentrations generally from 2.0 × 10^{-4} to 10.0 ×

10^{-4} M while the initial [Pt(IV)] and pH were held constant at 2.7 × 10^{-5} M and 4.7, respectively. The presence of [Cl$^-$] in the region (2–10) × 10^{-4} M does not affect the rate of oxidation. The rate of oxidation increases with an increase in the substrate concentration. Plots of $1/k_{obsd}$ against $1/[N_2H_5^+]$ at different temperatures are shown in Figure 1.

Effect of pH. The reaction was studied at different pH values ranging from 3.63 to 5.60 while the concentrations of substrate and oxidant and the ionic strength were kept fixed at 3.0 × 10^{-4} M, 2.76 × 10^{-5} M, and 0.20 M, respectively. Hydrogen ion has been found to have no effect on the rate at constant ionic strength.

Effect of Salts. The effects of addition of salts like sodium perchlorate and sodium chloride on the observed first-order rate constants were studied. Sodium perchlorate accelerates the rate of reaction (Table I) unlike sodium chloride which inhibits the rate of the oxidation although the inhibition at [NaCl] ≤ 1.0 × 10^{-3} M is not significant.

Effect of Solvent. Solvent effect was studied by varying the dielectric constant of the medium by the addition of dioxane. The rate decreases as the dielectric constant falls (Table II). The dielectric constants of the mixtures were calculated from the work of Akerlof and Short.[12] The plot of log k_{obsd} against $1/\epsilon$ (ϵ is the dielectric constant) yields a straight line.

Discussion

The oxidation of hydrazinium ion by platinum(IV) is independent of added hydrogen ion concentrations. A retarding effect on the rate would have been expected had equilibrium 2 been involved. Since the dissociation constant of hydra-

$$N_2H_5^+ \rightleftarrows N_2H_4 + H^+ \tag{2}$$

zinium ion is 1.02 × 10^{-8} at 25 °C, the substrate will remain as an undissociated form at pH 4.7. Recently ESR measurement[13,14] has indicated that protonated amines are attacked by electrophiles at a point farthest from the site of protonation and the electrophile would attack the unprotonated N atom in $N_2H_5^+$. Earlier reports[15,16] have also indicated that the oxidation of inorganic and organic compounds by platinum(IV) is brought about by $PtCl_6^{2-}$. It has been observed that the addition of sodium perchlorate to the reaction mixture accelerates the rate of reaction considerably whereas extraneous addition of sodium chloride to the reaction mixture inhibits the rate of reaction. The reaction may be explained according to the steps
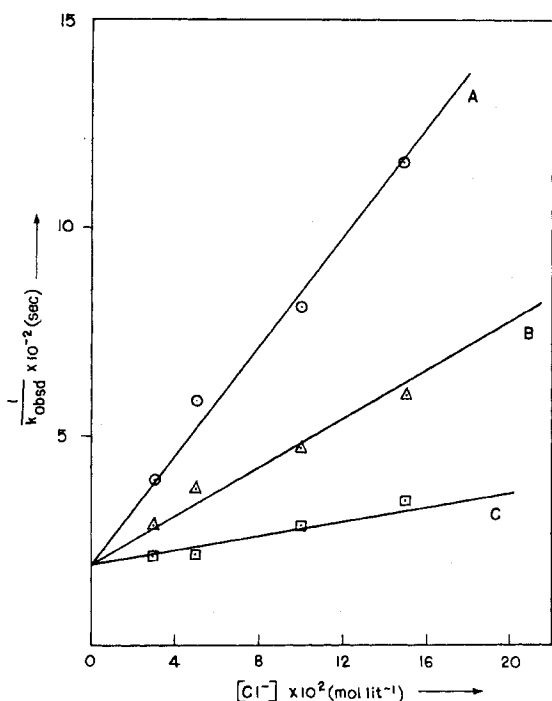
$$PtCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} PtCl_5^- + Cl^- \tag{3}$$

$$PtCl_5^- + N_2H_5^+ \overset{k_2}{\rightarrow} products \tag{4}$$

The rate expression would be

$$\frac{-d[PtCl_6^{2-}]}{dt} = \frac{k_1 k_2 [PtCl_6^{2-}][N_2H_5^+]}{k_{-1}[Cl^-] + k_2[N_2H_5^+]} \tag{5}$$

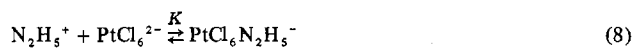Since most of the runs were carried out at a constant [Cl$^-$],

Figure 2. Plots of $1/k_{obsd}$ against [Cl⁻] at different constant [N₂H₅⁺] values; [Pt(IV)] = 2.76 × 10⁻⁵ M, pH 4.7, 30 °C. [N₂H₅⁺]: A, 1.0 × 10⁻³ M; B, 8.0 × 10⁻³ M; C, 12.0 × 10⁻³ M.

Table III. Effect of Acrylamide Concentrations on the Observed Pseudo-First-Order Rate Constant ([Pt(IV)] = 3.1 × 10⁻⁵ M, [N₂H₅⁺] = 2.5 × 10⁻⁴ M, pH 4.7)

[Acrylamide], M	0	0.006	0.012	0.024
$10^3 k_{obsd}$, s⁻¹	1.22	0.36	0.12	0.06

composition. The rate decreases with the increase in solvent composition (Table II) in the present reaction indicating that the chemical force rather than the electrostatic force of attraction may play a predominant role. Moreover, platinum(IV) demonstrates a coordination number of 7 in the complex which is unlikely. Consequently, the reaction via steps (8) and (9) seems improbable.

The oxidation of hydrazinium ion may lead to the initial formation of protonated diimide[16] (NHNH₂⁺) or protonated hydrazyl[18] (NHNH₃⁺) radical in solution depending upon whether platinum(IV) behaves as a 2- or 1-equiv oxidant. Hydrazinium ion has been shown to be oxidized by a 2-equiv oxidant to nitrogen by Beck et al.[17] whereas Cuy and his co-workers[5,6] from a study of the interaction of hydrazinium ion with 1-equiv oxidants such as iron(III) and manganese(III) concluded that simultaneous formation of N₂ and NH₄⁺ takes place according to the equation

$$N_2H_5^+ + M^{3+} \rightarrow \frac{1}{2}N_2 + NH_4^+ + H^+ + M^{2+} \tag{11}$$

the product k_{-1}[Cl⁻] is constant except in the limited number of runs in which [Cl⁻] was varied. Equation 5 may be arranged as

$$k_{obsd} = \frac{k_1 k_2 [N_2H_5^+]}{k_{-1} [Cl^-] + k_2 [N_2H_5^+]} \tag{6}$$

$$\frac{1}{k_{obsd}} = \frac{k_{-1} [Cl^-]}{k_1 k_2 [N_2H_5^+]} + \frac{1}{k_1} \tag{7}$$

Several series of runs, each series at a different fixed [N₂H₅⁺], were taken. In each series the [Cl⁻] was varied. For each series $1/k_{obsd}$ vs. [Cl⁻] is plotted (Figure 2). The lines make a common intercept of $1/k_1$. The absence of the effect of hydrogen ion concentration, observed effect of substrate concentration, and inverse chloride ion dependence on rate justify the postulated rate law (5). The reaction might also be approached by considering that a 1:1 intermediate compound is formed between PtCl₆²⁻ and N₂H₅⁺ followed by the decomposition of the intermediate compound to give products of reaction, i.e.

$$N_2H_5^+ + PtCl_6^{2-} \overset{K}{\rightleftharpoons} PtCl_6N_2H_5^- \tag{8}$$

$$PtCl_6N_2H_5^- \overset{k}{\rightarrow} products \tag{9}$$

The empirical rate law would then be

$$\frac{-d[PtCl_6^{2-}]}{dt} = \frac{kK[PtCl_6^{2-}] [N_2H_5^+]}{1 + K[N_2H_5^+]} \tag{10}$$

The plots of $1/k_{obsd}$ against $1/[N_2H_5^+]$ give straight lines making intercepts in the y axis (Figure 1). However, the equilibrium constants of the 1:1 intermediate compound are 6.04 × 10³, 3.88 × 10³, 2.17 × 10³, and 1.05 × 10³ M⁻¹ at 15, 20, 25, and 30 °C, respectively. The values are extraordinarily high for two ions associating only by electrostatic interactions. Again, for a reaction between ions of opposite charge, the rate would increase with the increase in the solvent
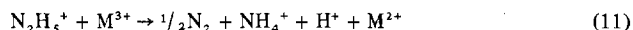
where M = Fe(III) and Mn(III). The oxidation of hydrazinium ion by platinum(IV) undergoing a two-electron change would lead to the formation of only one product, i.e., N₂. This is possible only when hydrazinium ion is oxidized to give protonated diimide and the latter is known to be a powerful reducing agent. The presence of both N₂ and NH₄⁺ in the reaction mixture indicates that platinum(IV) possibly behaves as a 1-equivalent oxidant and oxidizes hydrazinium ion to give the protonated hydrazyl radical and platinum(III). A number of platinum(III) compounds have been reported in the literature[19] although there appears to be no proof that they actually contain platinum(III) rather than platinum(II) and platinum(IV). The intermediate formation of platinum(III) in solution has been postulated in various reactions involving the platinum(II)–platinum(IV) redox couple notably in certain photochemical and catalyzed substitution reactions.[20–22] The evidence for the intermediate formation of platinum(III) has been demonstrated by Halpern and Pribanic[23] in the oxidation of platinum(II) complexes by hexachloroiridate. However, in the present study the addition of acrylamide to the reaction mixture gave a cloudy suspension on standing for few minutes indicating that a reducing species is formed in solution. The rate of oxidation was also retarded by the addition of acrylamide (Table III). It is suggested that polymer when formed may preferentially adsorb one of the reactants and so reduce abnormally its bulk concentration in aqueous phase. Platinum(III) may further react with another N₂H₅⁺ ion to give more NHNH₃⁺ and platinum(II) or may disproportionate to give platinum(II) and regenerate platinum(IV). Two protonated hydrazyl radicals may decompose to give finally products of oxidation, e.g., N₂ and NH₄⁺.

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Kinetics and Mechanism of Electron-Transfer Reactions of Aquothallium(III) and Coordinated Thallium(III). 13. Reduction of Thallium(III) by Nitrous Acid in Perchloric Acid Solution

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The reaction between thallium(III) and nitrous acid has been studied at 25 °C in acid perchlorate media. The stoichiometry of the reaction corresponds to the equation $Tl(III) + HNO_2 + H_2O \rightarrow Tl(I) + NO_3^- + 3H^+$. Thallium(III) probably forms three complexes, $TlNO_2^{2+}$, $Tl(NO_2)_2^+$, and $Tl(NO_2)_3$, and the reduction of Tl^{III} occurs via an internal redox reaction of $Tl(NO_2)_2^+$. The complete rate law for the reaction for $[HNO_2] > [Tl^{III}]$ is $-d[Tl^{III}]/dt = kK_2[HNO_2][H^+][Tl^{III}]/([H^+]^2 + K_2[H^+][HNO_2] + K_2K_3[HNO_2]^2)$, where k is the rate constant for the rate-determining step and K_2 and K_3 are the second and third successive formation constants for Tl^{III}–HNO$_2$ complexes. k was found to be $(3.9 \pm 0.1) \times 10^{-3}$ s^{-1} at 25 °C and $I \simeq 0.3$ M. Kinetic values of K_2 and K_3 were found to be 653 ± 24 and 6.9 ± 0.3, respectively, at 25 °C and $I \simeq 0.3$ M from the variation of the rate on the concentrations of nitrite and perchloric acid. The energy and entropy of activation for the rate-determining step were found to be 18.2 ± 1.0 kcal mol^{-1} and -10.4 ± 4.0 cal deg^{-1} mol^{-1}, respectively. The rate increases with increasing ionic strength but is strongly inhibited by chloride ions. Added thallium(I) and nitrate have no effect on the rate.

Introduction

A number of papers have appeared on oxidations by thallium(III) from this laboratory. Among the nitrogen reductants studied are hydroxylamine[1] and hydrazine.[2,3] Interest in the oxidation of nitrite arose because it is one of the products of oxidation of hydroxylamine and it is likely to form complexes with thallium(III). Nitrous acid is known to act as an oxidant as well as reductant. As an oxidant its reactions with SO_3^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$, $HCOO^-$, I^-, ClO_3^-, Fe^{2+}, NO^{2-}, and $SO_3NH_2^-$ have been reported.[4] Kinetics studies of reactions in which nitrite is a reducing substance seem to be few. Oxidations of nitrite by 1-equiv oxidants like cobalt(III)[5] and manganese(III)[6] are accompanied by the intermediate formation of the $NO_2\cdot$ radical. There is evidence for intermediate complex formation in the oxidation by chromium(VI).[7] In oxidations by Caro's acid, peroxyacetic acid, and hydrogen peroxide, nucleophilic displacement of oxygen by nitrite has been proposed.[8] Oxidation by hypochlorite[9] has also been studied. The present study, apart from giving the kinetics behavior, is likely to throw light on the nature of the complexes of thallium(III) with nitrite.

Experimental Section

Stock solutions of thallic perchlorate and lithium perchlorate were prepared as described.[1] Nitrite was used in the form of its sodium salt (BDH, AnalaR). Solutions of nitrite were prepared daily although no appreciable decomposition occurred even in 2 days as also reported by earlier workers.[16] These solutions were standardized[11] with cerium(IV) and back-titrated with iron(II). Perchloric acid was 60% Riedel AnalaR. All other chemicals were either BDH AnalaR or GR Merck quality. Solutions were prepared in twice-distilled water, the second distillation being from potassium tetraoxomanganate(VII) solution.

Kinetics experiments were carried out in a temperature-controlled (± 0.1 °C) water bath. Nitrite was always the last component to be

added. The reaction was followed by measuring thallium(III) iodometrically.[12] When the concentration of thallium(III) used was low, it was determined colorimetrically.[13] The reaction was quenched by mixing the aliquots with a solution of HCl since thallium(III) forms strong complexes[14] with chloride which are not reactive. Since nitrite interferes in the determination of Tl^{III}, it was decomposed by the addition of urea before carrying out the iodometric determination.

In a few experiments, the rate was followed by determining nitrite cerimetrically[11] (back-titration being performed in sulfuric acid medium). The results obtained by this method were within 5% of those obtained iodometrically, and this shows that the decomposition of nitrite, if any, is within experimental error limits. However, in cases where the ratio $[NO_2^-]/[Tl^{III}]$ was large (5 times or more), 5–20% decomposition occurred in 2 half-lives. A separate study of the rate of decomposition of nitrous acid under similar conditions showed that it is negligible for the initial period of the reaction. The decomposition, therefore, was not taken into consideration.

The treatment of data is based on the initial rates obtained by the plane mirror method.[15] Duplicate rate measurements were reproducible to $\pm 5\%$.

Colorimetric measurements were made in a Spectronic 20 spectrophotometer at 380 nm. Absorption studies of nitrite solutions and mixtures of thallium(III) and nitrite were made in a Beckman DU spectrophotometer using 1-cm cells in the range 290–410 nm. Each observation on reaction mixtures was taken immediately after mixing fresh reactant solutions.

Results

The acid dissociation constant[16] of HNO_2 at 30 °C is 6×10^{-4} M; hence at the perchloric acid concentrations employed in the present investigation, nitrite is predominantly present as HNO_2.

Stoichiometry. Thallium(III) and nitrite in suitable acid medium were kept for ca. 24–48 h. Excess thallium(III) was then determined iodometrically.[9] In case of excess nitrite the usual procedure was not followed since free nitrous acid