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Kinetics and mechanism of the ferrate oxidation of hydrazine and monomethylhydrazine

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Abstract

The kinetics of the reaction of ferrate, FeO_4^{2-}, and hydrazines in aqueous media have been investigated and the results are reported. It was found that ferrate rapidly oxidizes hydrazine to molecular nitrogen and monomethylhydrazine to molecular nitrogen and methanol. The rate law for the reaction is first order with respect to each reactant and first order with respect to the hydrogen ion concentration. A two-electron pathway is proposed for each reaction. The generation of diazene as reaction intermediate was demonstrated for the oxidation of hydrazine.

Keywords: Kinetics and mechanism; Oxidation; Hydrazine; Ferrate complexes

1. Introduction

Although the ferrate ion, FeO_4^{2-}, has been known for over a century, its chemistry has remained relatively unexplored [1]. Ferrate is a tetrahedral ion and isostructural with chromate or permanganate [2]. It is a strong oxidant with reduction potentials of 0.9 and 1.9 V (versus NHE) in basic and acidic media, respectively [3]. The oxidations of a few organic substrates have been reported, all from a synthetic perspective. Aqueous potassium ferrate oxidizes alcohols to aldehydes or ketones [4], thiols to disulfides or sulfonic acids [5], aromatic amines to azo compounds [6] and 1° aliphatic amines deaminate to form aldehydes [4]. Solid barium ferrate was shown to convert phenylhydrazines into biphenyls in aprotic solvents [7]. The products and yields of all these reactions depend upon reaction times and conditions. It is interesting that, unlike its cogeners, permanganate and chromate, ferrate is unreactive toward addition across double or triple bonds. Such distinct reaction preferences should make ferrate an important and selective oxidant for synthetic organic studies.

In addition, with current and forthcoming environmental concerns, ferrate represents an ideal substitute for other oxidants, particularly chromate and chlorine. Doubtless the neglect of ferrate chemistry has been due to synthetic difficulties. We are currently engaged in the development of an alternative synthetic procedure that is simpler and produces a purer crude product [8].

To date, only a handful of kinetic studies of ferrate oxidations appears in the literature [9–12]. This is in sharp contrast to the number of studies with permanganate and chromate. Murmann and Goff [9] reported the first kinetic investigation in 1971 for the ferrate oxidation of hydrogen peroxide and sulfite along with the oxygen exchange study. Their sulfite work has been recently re-investigated by Johnson and Bernard [10] and found to be different than originally reported. In addition, Johnson reported the oxidation of selenite and found evidence for a quasi-stable ferrate/selenite bridged intermediate. Bielski et al. [11] have reported the ferrate oxidation of amino acids and a pulsed-radiolytic study of the ferrate reduction by the hydrated electron to form $Fe(V)_{aq}$.

Carr et al. have also studied ferrate oxidations and their application to waste water treatment [12]. It is probably in this venue that ferrate holds its greatest promise for industrial application. There has been a number of studies investigating the applicability of ferrate in waste treatment which involve not only its oxidative abilities, but also its floc formation and disinfective properties. It is because of ferrate's remediative

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facilities that we have investigated the reaction of ferrate with hydrazine and monomethylhydrazine. Both of these reductants are used in the design and testing of rocket propulsion systems. How to deal with the unused fuels is a problem and ferrate has been suggested as a remedy. The kinetics and mechanism for these reactions are reported.

2. Experimental

2.1. Materials

The hydrazine hydrate and monomethylhydrazine were purchased from Aldrich Chemicals. Their purities were checked by gas chromatography (flame ionization) and found to be satisfactory. The concentrations of the aqueous solutions used for the kinetic and stoichiometric studies were determined by titration with chromate.

Potassium ferrate was prepared by a slight modification of the method reported by Thompson et al. [13]. The crude product was recrystallized and the purity checked by spectrophotometric analysis at 505 nm ($\epsilon = 1100$ M^{-1} cm^{-1}) [14]. Purities up to 95% were obtained and the measured rates were found to be independent of the sample purity.

Stock solutions of the reductants were prepared using deionized water. Ionic strength was maintained with sodium perchlorate, and sodium phosphate buffers were used to control pH. The phosphate ion also prevented precipitation of iron hydroxides, which are produced during the reduction process. Solutions were bubbled with argon gas to remove dissolved oxygen from solution where indicated.

2.2. Kinetic measurements

The reaction rates were measured spectrophotometrically using a D110 Durrum spectrophotometer with an OLIS computer interface. The reactions were monitored at 505 nm and pseudo-first-order conditions with the reductant in excess were employed throughout. The exponential absorbance decays were fitted using an OLIS fitting routine (Sci-Fit). Each rate constant is an average of three to five trials. The temperature was controlled to within 0.1 °C. For determination of the activation parameters, four temperatures ranging from 5.1 to 25 °C were used. All studies were conducted using 0.05 M phosphate buffers to control pH and to prevent any precipitation of iron hydroxide/oxides by complexation of the iron final product.

2.3. Trapping studies

Valeric acid and 4-pentenoic acid were purchased from Aldrich. Their purities were checked using gas chromatography and found to only give one peak on the chromatograph.

3. Results and discussion

3.1. Oxidation of hydrazine

3.1.1. Stoichiometry

Ferrate reacts rapidly (<1 s) with hydrazine in aqueous solution and gas bubbles are evolved from the solution during reaction. The gas evolved was identified using mass spectroscopy as molecular nitrogen. When carried out under aerobic conditions, ferric oxide precipitates from solution. The presence of Fe(III) was demonstrated by the addition of potassium thiocyanate to form the red ferric thiocyanate complex. Under anaerobic conditions however the spent reaction mixtures give no coloration upon addition of thiocyanate, which indicates absence of Fe(II). The addition of phenanthroline produces the characteristic red color of ferrous phenanthroline complexes. We conclude therefore that Fe(II) and nitrogen are the final products when hydrazine is in excess and oxygen is excluded.

The reaction stoichiometry was determined under anaerobic conditions with hydrazine in excess. A $1.1 \pm 0.15:1$ stoichiometry was determined for hydrazine to ferrate by titration of the excess hydrazine in the spent reaction mixture with standardized dichromate. The stoichiometry is pH independent between 7.5 and 11.0. Based on the above information, the following reaction may be written.

$$FeO_4^{2-} + N_2H_4 \longrightarrow Fe(II) + N_2 + 4OH^- \quad (1)$$

Upon addition of oxygen to the spent mixture, the Fe(II) was rapidly oxidized to Fe(III) whereupon it precipitated from solution as ferric oxide.

3.1.2. Kinetics

The reaction kinetics were studied anaerobically and under pseudo-first-order conditions with hydrazine in excess. For these studies the ferrate concentrations were maintained low enough so that bubble formation was not observed in the observation chamber of the stopped-flow spectrophotometer. The absorbance decreases (505 nm) for the loss of ferrate fit nicely to a simple exponential decay. Fig. 1 shows a typical plot of the observed rate constants versus the hydrazine concentration at constant pH. The linear dependence indicates a first-order hydrazine term in the rate law. The positive intercept (approximately 2 s^{-1}) is due to the ferrate oxidation of solvent water in the absence of hydrazine. Similar intercepts have been observed in other ferrate studies [10].

The second-order observed hydrazine rate constants were measured at different hydrogen ion concentrations;

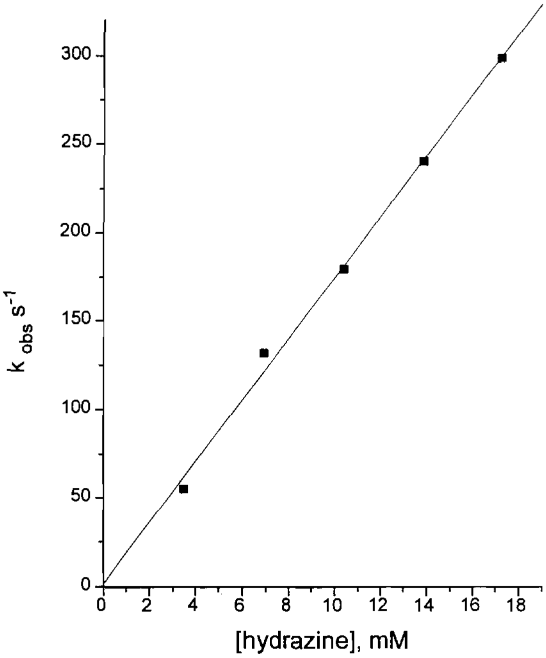

Fig. 1. A typical plot of k_{obs} vs. [hydrazine]. Conditions: pH = 8.5, T = 25.0 °C, I = 1.0 M ($NaClO_4$), 0.05 M (Na phosphate) buffer.

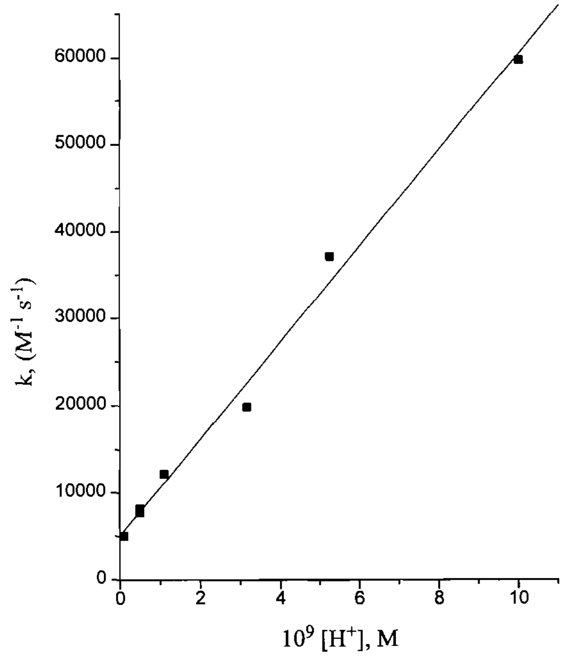

Fig. 2. The hydrogen ion dependence on the rate of the hydrazine/ferrate reaction.

almost no effect on the rate constants was observed upon increasing the phosphate buffer concentration from 0.05 to 0.10 M. Fig. 2 shows first-order dependence on H^+ with the positive y-intercept indicating an acid independent term. A rate law may be written as follows:

$$-d[Fe(VI)]/dt = (k_0 + k_H[H^+])[FeO_4^{2-}][N_2H_4] \qquad (2)$$

The values for k_0 and k_H are $(5.05 \pm 0.09) \times 10^3$ M^{-1} s^{-1} and $(5.65 \pm 0.18) \times 10^{12}$ M^{-2} s^{-1}, respectively, at 25 °C. The temperature dependence of this reaction was studied at several pHs to obtain the activation parameters of ΔH^* and ΔS^* for both k_0 and k_H. These are 19.7 ± 3.3 and 6.60 ± 2.1 kcal mol^{-1} and 24.3 ± 8.2 and 25.1 ± 6.9 cal mol^{-1} K^{-1}, respectively. The activation parameters for k_H are actually a composite of the activation enthalpy and entropy for electron transfer and the acid protonation enthalpy and entropy of the hydrazinium ion. According to Martell and Smith [15], ΔH and ΔS for the hydrazinium acid dissociation constant are −9.7 kcal mol^{-1} and +4 cal mol^{-1} K^{-1}. This leads to $\Delta H^{*\prime}$ and $\Delta S^{*\prime}$ for electron transfer as 16.3 kcal mol^{-1} and 22 cal mol^{-1} K^{-1}.

The simplest mechanism for this reaction would involve a direct four-electron oxidation of the hydrazine by ferrate to produce the final products. Although such multi-electron redox reactions may be possible, two-electron pathways are well documented for hydrazine oxidations and such a mechanism is more likely in place. Chemical trapping studies also support an alternative pathway to a single four-electron step.

When molecular nitrogen is the product of the oxidation of hydrazine, a two-electron initial oxidation is generally in operation [14] as found with chromate and permanganate [16]. In contrast, a one-electron initial oxidation generally produces ammonia [14]. Since nitrogen is the final product for the ferrate oxidation, a two-electron rate determining step has been invoked. A mechanism consistent with the rate law and the final products is shown in Scheme 1. The charges are not balanced in Scheme 1 since the formula of the Fe(IV) intermediate is unknown. Based on this mechanism, the rate constant k_H is actually a composite of $k_1K_a^{-1}$. The pK_{a1} for hydrazinium ion is 8.18 which leads to a value of k_1 equal to 3.6×10^4 M^{-1} s^{-1}, which is approximately an order of magnitude greater than the acid independent term.

$$N_2H_5^+ \overset{K_a}{\rightleftharpoons} N_2H_4 + H^+ \qquad (3)$$

$$FeO_4^{2-} + N_2H_4 \xrightarrow{k_0} Fe(IV) + N_2H_2 + 2OH^- \qquad (4)$$

$$FeO_4^{2-} + N_2H_5^+ \xrightarrow{k_1} Fe(IV) + N_2H_2 + 3OH^- \qquad (5)$$

$$Fe(IV) + N_2H_2 \longrightarrow Fe(II) + N_2 + 2OH^- \qquad (6)$$

$$Fe(VI) + N_2H_2 \longrightarrow Fe(II) + N_2 + 2H^+ \qquad (7)$$

Scheme 1.

In each rate limiting step, diazene, N_2H_2, is the suggested nitrogen intermediate. This species has been observed or postulated in a variety of hydrazine oxidations [17–20] and is usually, although not absolutely, indicative of a initial two-electron oxidation of hydrazine.

Diazene is a powerful reductant, especially for unsaturated hydrocarbons and diazo compounds.

$$N_2H_2 + RCH{=}CH_2 \longrightarrow N_2 + RCH_2CH_3 \qquad (8)$$

We therefore attempted to trap this intermediate species [16] by taking advantage of the fact that the reaction of ferrate with alkenes is very slow, if it reacts at all. An aqueous solution (pH = 9, $NaHCO_3$ buffer) containing 4-pentenoate and a ten-fold excess of hydrazine was added to an aqueous solution of potassium ferrate, equimolar with respect to the hydrazine. The rust brown product mixture was acidified to pH 1 with dilute HCl and extracted with diethyl ether. The gas chromatogram (DB Wax, 30 m column) of the extract showed two peaks, one due to unreacted pentenoic acid and another small peak having the same retention time as valeric acid. The identity of these species was confirmed using GC-MS. The per cent hydrogenation was about 20%, which is in line with other trapping studies. This evidence demonstrates that diazene is generated during the ferrate oxidation of hydrazine since treatment of 4-pentenoic acid with hydrazine alone does not produce valeric acid.

$$FeO_4^{2-} + N_2H_4 \longrightarrow Fe(IV) + N_2H_2 \qquad (9)$$

$$N_2H_2 + CH_2{=}CHCH_2CH_2CO_2^- \longrightarrow N_2 + CH_3CH_2CH_2CH_2CO_2^- \qquad (10)$$

Although few detailed mechanistic studies of ferrate oxidation exist for comparison, two-electron steps appear to be the favored pathway for ferrate oxidations. In the chromate oxidation of hydrazine, the initial formation of a chromate–hydrazine ester was proposed by Haight et al. based on saturation kinetics [16]. This intermediate then undergoes electron transfer to produce the final products. Similar mechanisms have also been suggested for the vanadate and molybdate oxidation of hydrazines [21,22]. Although the formation of an 'inner-sphere' intermediate in ferrate oxidations has been proposed by Murmann and Goff [9] and later by Johnson and Bernard [10] for the ferrate oxidation of sulfite and selenite, there is no kinetic evidence for such an intermediate in the present study. Rapid scanning spectrophotometry also provides no spectral evidence for an intermediate. Finally, the rate of oxygen substitution on the ferrate center is slow compared to the oxidation rates, which should preclude formation of an $O_3FeNH_2NH_2$ intermediate as seen in other hydrazine oxidations. Based on these arguments, we tentatively invoke an outer-sphere pathway.

The activation enthalpies for this reaction are similar to those for chromate/hydrazine reactions, $\Delta H = 7.32$ kcal mol^{-1} whereas the activation entropies are of similar magnitude but opposite in sign, $\Delta S = -11.8$ cal mol^{-1} K^{-1} [16]. In view of the complexity of these reactions and the sparsity of other ferrate/substrate kinetic and thermodynamic data, these values are difficult to interpret.

3.2. Oxidation of monomethylhydrazine

3.2.1. Stoichiometry

As with hydrazine, ferrate rapidly reacts with excess monomethylhydrazine, MMH. Gas evolution was observed during the reaction and it was identified as molecular nitrogen using mass spectrometry. No other gaseous products were found. The carbon containing final product was identified as methanol using GC-MS. The oxidation state of iron was determined as in the hydrazine study and found to be Fe(II) under anaerobic conditions. Based on these observations, the following reaction may be written:

$$H_2O + FeO_4^{2-} + CH_3NHNH_2 \longrightarrow Fe(II) + CH_3OH + N_2 + 4OH^- \qquad (11)$$

When oxygen was added to the spent reaction mixture, the Fe(II) was rapidly oxidized to Fe(III) whereupon it precipitated from solution as ferric oxide.

When ferrate is in excess, the methanol produced by the above reaction is slowly oxidized to formaldehyde and, contrary to the literature [4], formate. These secondary reactions however are slow compared to the ferrate/MMH reaction and are not important to the present study since MMH is always maintained in excess.

3.2.2. Kinetics

The reaction kinetics were studied anaerobically and under conditions analogous to those in the hydrazine study. The absorbance decreases (505 nm) for the loss of ferrate were fitted to a simple exponential decay. Fig. 3 shows a typical plot of the observed rate constants versus the MMH concentration at constant pH. The linear dependence indicates a first-order MMH term and the positive intercept was assigned to the ferrate oxidation of solvent water in the absence of substrate.

The second-order rate constants, obtained from the slopes of the above plots, were measured at different hydrogen ion concentrations. Fig. 4 shows a first-order dependence on $[H^+]$ with the positive y-intercept which indicates an acid independent term. A rate law may be written as follows:

$$-d[Fe(VI)]/dt = (k_{0M} + k_{MH}[H^+])[FeO_4^{2-}][MMH] \qquad (12)$$

The values for k_{0M} and k_{MH} are $(4.41 \pm 0.55) \times 10^3$ M^{-1} s^{-1} and $(9.79 \pm 0.14) \times 10^{12}$ M^{-2} s^{-1}, respectively, at 25 °C. The activation parameters of ΔH^* and ΔS^* for k_{0M} and k_{MH} are 16.8 ± 2.3 and 5.28 ± 0.51 kcal mol^{-1} and 14.0 ± 3.9 and 40.6 ± 11.6 cal mol^{-1} K^{-1}, respectively. As described for the hydrazine system, the values

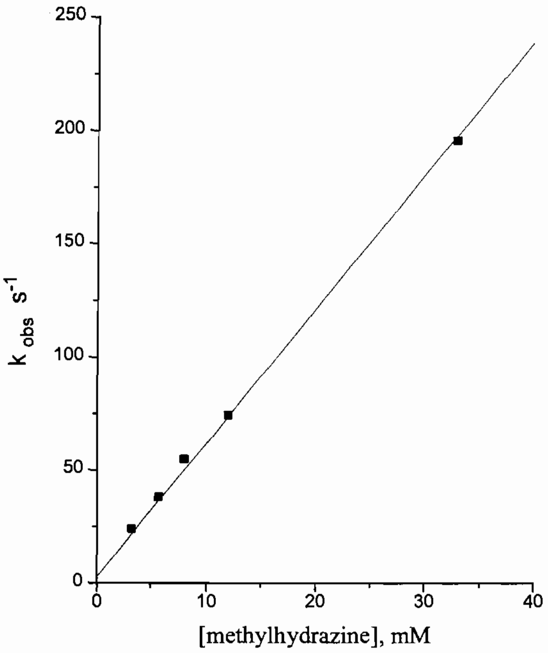

Fig. 3. A typical plot of k_{obs} vs. [methylhydrazine]. Conditions: pH = 9.7, T = 25.0 °C, I = 1.0 M (NaClO$_4$), 0.05 M (Na phosphate) buffer.

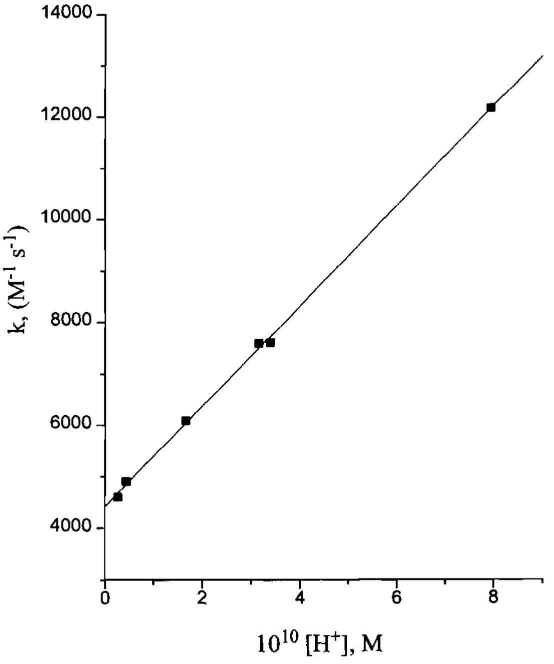

Fig. 4. The hydrogen ion dependence on the rate of the methylhydrazine/ferrate reaction.

$$N_2H_5^+ \overset{K_a}{\rightleftharpoons} N_2H_4 + H^+ \tag{13}$$

$$FeO_4^{2-} + CH_3N_2H_3 \xrightarrow{k_{0M}} Fe(IV) + CH_3N_2H + 2OH^- \tag{14}$$

$$FeO_4^{2-} + CH_3N_2H_4^+ \xrightarrow{k_{1M}} Fe(IV) + CH_3N_2H + 4OH^- \tag{15}$$

$$FeO_4^{2-} + CH_3N_2H \longrightarrow Fe(II) + CH_3N_2^+ + 4OH^- \tag{16}$$

$$Fe(IV) + CH_3N_2H \longrightarrow Fe(II) + CH_3N_2^+ + H^+ \tag{17}$$

$$CH_3N_2^+ + H_2O \longrightarrow CH_3OH + H^+ + N_2 \tag{18}$$

Scheme 2.

of ΔH^* and ΔS^* for the hydrazinium pathway are composite terms.

Since ferrate appears to favor a two-electron pathway, a mechanism consistent with the rate law may be written as shown in Scheme 2. Although the pK_a for methylhydrazine has not, to our knowledge, been reported, it should be similar to that of hydrazine. Using this assumption, the value for k_{1M} may be estimated as 5×10^4 M^{-1} s^{-1}. This shows that protonation significantly enhances the reactivity of MMH to the same degree as hydrazine.

Analogous with the hydrazine study, the rate determining steps probably produce methyldiazene which undergoes another $2e^-$ oxidation to give diazomethane. Trapping experiments to demonstrate the existence of $CH_3N_2^+$ by methylation of a carboxylate ion or secondary amine were unsuccessful.

4. Conclusions

Ferrate is a potent oxidant for hydrazine and MMH which are both converted rapidly and quantitatively into molecular nitrogen and, for the latter, methanol. In each case a two-electron outer-sphere pathway is postulated to form the corresponding diazene. Based on data for other Fe(VI) oxidation studies, initial two-electron oxidations appear to be a general feature of ferrate oxidations. The diazene intermediate is subsequently oxidized to the final product by either another ferrate ion or the Fe(IV) intermediate produced in the initial step. Fe(IV) has been shown to be an even more effective oxidant than ferrate [11]. We are currently pursuing kinetic studies of the oxidation of aromatic hydrazines along with the symmetrical and unsymmetrical dimethylhydrazines with ferrate.

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