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Oxidation of Methylhydrazine by Cerium(IV) in Acid Media

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The oxidation of methylhydrazine, $CH_3N_2H_3$, by Ce(IV) in acid media was studied. When the mole ratio $CH_3N_2H_3$:Ce(IV) was ≥4 the mole ratio of N_2 evolved to Ce(IV) consumed was 1:4. Two possible stoichiometric equations are given which result in the observed stoichiometry. A detailed kinetic study of this reaction using the stopped-flow technique showed that the reaction obeyed the rate expression $-d[\mathrm{Ce(IV)}]/dt = k_H[\mathrm{Ce(IV)}][CH_3N_2H_4^+]$. The second-order rate constant, k_H, was found to be hydrogen ion dependent and cerous ion independent. Two possible rate-determining steps consistent with our data are presented.

Introduction

Many workers have studied the oxidation of hydrazine by a variety of oxidizing agents. Cahn and Powell[1] studied this reaction using iodate, IO_3^-; ferricyanide, $Fe(CN)_6^{3-}$; ceric, Ce(IV); and several other oxidizing agents. These workers studied this reaction using labeled hydrazine (^{15}N), the emphasis of their study being on the stoichiometry of the reaction. Although they studied the kinetics of the Fe(III) oxidation of N_2H_4, a detailed kinetic study was not undertaken. Higginson and Wright[2] and later Rosseinsky[3] did a more detailed kinetic study of the Fe^{III}–N_2H_4 reaction. Browne[4] and Bray[5] and co-workers found three distinct reactions involving one-, two-, and four-electron changes per mole of hydrazine. As early as 1924 Cuy[6] showed that almost invariably the oxidation of hydrazine resulted in the evolution of a gaseous product, usually nitrogen.

More recently Davies and Kustin[7] studied the stoichiometry and kinetics of the oxidation of hydrazine and the five possible methyl derivatives of hydrazine by manganese(III). They found that Mn(III) oxidizes methylhydrazine according to the equation:

$$4Mn^{III} + 2CH_3N_2H_4^+ \rightarrow (CH_3)_2N_4H_4^{2+} + 4Mn^{II} + 4H^+$$

with no evolution of nitrogen.

The results of this study yield a rate expression for the Ce^{IV}–$CH_3N_2H_3$ reaction which is identical in form with that found by Davies and Kustin for the Mn^{III}–$CH_3N_2H_3$ but indicate that a different mechanism is involved since N_2 gas is evolved.

Experimental Section

Reagents. Triply distilled water was used in the preparation of all solutions.

Fisher Certified Reagent Grade cerium(IV) ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, was used in the preparation of Ce(IV) solutions.

Methylhydrazine, $CH_3N_2H_3$ (Aldrich Chemical, 98% in H_2O), was used in the preparation of the $CH_3N_2H_3$ solutions. It was diluted and analyzed by pH titration with previously standardized HCl solution. The solutions were acidified using Baker reagent grade $HClO_4$.

Stoichiometry. A dual buret gas analyzer apparatus previously described was used.[8]

Solution Preparation. Methylhydrazine solutions were prepared as above, that is, solutions of the desired acidity were immediately acidified with perchloric acid to the desired value. While this was also true for most of the Ce(IV) solutions (except where noted in the text) a limited number of runs were carried out where the Ce(IV) was first dissolved in water rather than perchloric acid solutions. These aqueous nonacidified Ce(IV) solutions were then allowed to age for specified times prior to their being acidified and then the stoichiometric Ce(IV):N_2 mole ratio was determined using the dual gas buret analyzer apparatus.

Kinetic Measurements. Rates of reaction were followed by measuring the change in absorbance of Ce(IV) at 300 nm using the Aminco-Morrow stopped-flow apparatus[9] attached to an Aminco minimonochromator. The detector used was an R-136 Hamamatsu photomultiplier (PMT) powered by a Harrison 6515A dc Power Supply. The PMT output was fed into the Aminco kinetic photometer and the logarithmic (absorbance) signal was then displayed using the Tektronix 564B storage oscilloscope.

Table I. N_2:Ce(IV) Mole Ratio[a]

Expt No.	Moles of Ce(IV)[b] × 10^4	Moles of $CH_3N_2H_3$	Ce(IV): $CH_3N_2H_3$	Moles of N_2 × 10^4	N_2: Ce(IV)
1	4.11	18.5	1:4.15	1.01	1:4.09
2	4.00	18.5	1:4.62	1.05	1:3.89
3	3.32	332	1:100	0.80	1:4.15
4	3.32	116	1:50.0	0.84	1:3.95
5	7.93	55.4	1:7.07	3.02	1:3.92
6	4.00	18.5	1:4.62	1.00	1:4.00
7	6.00	37.0	1:6.15	1.55	1:3.87
8	6.00	37.0	1:6.15	1.43	1:4.19
9	5.00	37.0	1:7.40	1.19	1:4.18

[a] All runs were performed at 25 °C. [b] In experiments 1 through 5, $[HClO_4] = 1.00$ M; in experiments 6 and 7, $[HClO_4] = 2.00$ M; in experiments 8 and 9, $[HClO_4] = 5.00$ M.

Results and Discussion

Mass spectrometric analysis of the gaseous product of the reaction between Ce(IV) and methylhydrazine showed that nitrogen was liberated.

Table I gives the results of the stoichiometry determination when the quantity of methylhydrazine was in excess over that of Ce(IV). This is analogous to the conditions used in the kinetic runs where the methylhydrazine concentration was approximately a hundredfold greater than that of the cerium(IV) concentration. Under these experimental kinetic conditions a constant mole ratio of nitrogen:cerium(IV) of 1:4 was obtained consistent with two possible reactions,

$$4Ce^{IV} + 2CH_3N_2H_3 \rightarrow 4Ce^{III} + (CH_3)_2N_2H_2 + N_2 + 4H^+ \qquad (1)$$

or

$$4Ce^{IV} + CH_3N_2H_3 + H_2O \rightarrow 4Ce^{III} + CH_3OH + N_2 + 4H^+ \qquad (2)$$

In addition, either of the above reactions plus the following is also consistent;

$$2CH_3N_2H_3 \rightarrow (CH_3)_2N_2H_2 + N_2H_4$$

The stoichiometric ratios were independent of the acidity.

Although methylhydrazine is written in reactions 1 and 2 as $CH_3N_2H_3$, it is a basic molecule and exists primarily as $CH_3N_2H_4^+$ in acidic media.

When the Ce(IV) was placed in excess over the methylhydrazine the N_2:$CH_3N_2H_3$ mole ratio was constant at 1:1 and was reproducible to within ±3% for Ce(IV):$CH_3N_2H_3$ mole ratios of 10:1 to 15:1 (Table II). In these runs the $CH_3N_2H_3$ was added to the Ce(IV) solution thus preventing the methylhydrazine from being in excess over the cerium.

Table II. N_2:$CH_3N_2H_3$ Mole Ratio[a]

Moles of $CH_3N_2H_3$ × 10^4	Moles of Ce(IV) × 10^4	Ce(IV): $CH_3N_2H_3$	Moles of N_2 × 10^4	N_2: $CH_3N_2H_3$
2.96	29.9	10.1:1	2.94	1:1.01
2.96	35.2	11.9:1	2.85	1:1.04
2.96	45.0	15.2:1	2.59	1:1.14

[a] All runs were performed at 25 °C. The $[HClO_4] = 1$ M in all solutions.

Table III.[a] Effect of Ce(IV), $CH_3N_2H_3$, and Ce(III) on k_{obsd}

[Ce-(IV)] × 10^4	(CH_3-N_2H_3) × 10^2	[Ce-(III)]$_0$ × 10^2	k_{obsd},[b] s^{-1}	k_H, M^{-1} s^{-1}
3.29	2.03	0.00	0.0894	4.36
5.53	4.06	0.00	0.183	4.51
5.46	3.70	0.00	0.173	4.67
5.15	5.55	0.00	0.247	4.45
3.29	9.25	0.00	0.433	4.67
5.53	10.0	0.00	0.433	4.33
5.46	3.70	0.00	0.73	4.67
7.15	3.70	0.00	0.173	4.67
5.15	5.55	0.00	0.247	4.45
2.41	5.55	0.00	0.247	4.45
3.90	9.25	0.00	0.420	4.54
3.90	9.25	0.90	0.420	4.54
3.90	9.25	4.46	0.433[c]	4.67
3.90	9.25	9.25	0.420[c]	4.54

[a] In all runs $[HClO_4]_0 = 1.0$ M. [b] Each value of k_{obsd} is the result of at least three replicate runs. [c] In these runs the loss of Ce(IV) was followed at 350 nm. This was done to minimize the absorbance of Ce(III) which at the concentration used in these runs was appreciable at 300 nm.

Table IV. Variation of k_H with Acidity

[Ce IV] × 10^4	$[CH_3N_2H_3]_0$ × 10^2	$[HClO_4]_0$	k_H,[a] M^{-1} s^{-1}
5.06	7.40	0.656	4.92
4.43	7.40	1.13	3.91
4.70	7.40	1.81	3.23
4.98	7.40	2.28	2.43
4.78	7.40	3.45	1.88

[a] In these experiments $[Ce(III)]_0 = 0.0$.

From the data it is apparent that if reaction 1 is occurring then a different mechanism is at work when the Ce(IV) is placed in excess over methylhydrazine. Reaction 2 however accounts for the stoichiometry under all conditions. All kinetic runs were carried out with the $CH_3N_2H_3$ in excess over cerium(IV).

Table III contains the first-order rate constants, k_{obsd}, defined (at constant $[H^+]_0$ and $[CH_3N_2H_4^+]_0$) by

$$-d[Ce(IV)]/dt = k_{obsd}[Ce(IV)] \tag{I}$$

The second-order rate constant, k_H, defined by

$$k_H = k_{obsd}/[CH_3N_2H_4^+]_0 \tag{II}$$

was constant at 4.5 ± 0.1 M^{-1} s^{-1}. This second-order rate constant was found to be cerous ion and ionic strength independent but was dependent upon the acidity.

Hydrogen Ion Dependency and Mechanism. Table IV gives the effect of acidity upon k_H. These results may be explained in terms of reactions 3 and 4 being rate determining. The

$$Ce^{4+} + CH_3N_2H_4^+ \rightarrow Ce^{3+} + CH_3N_2H_3\cdot^+ + H^+ \quad (k_3) \tag{3}$$

$$CeOH^{3+} + CH_3N_2H_4^+ \rightarrow Ce^{3+} + CH_3N_2H_3\cdot^+ + H_2O \quad (k_4) \tag{4}$$

assumption is made that all protolytic steps are rapid with respect to these reactions. In both reactions the $CH_3N_2H_3\cdot^+$ free radical is produced and then rapidly consumed.

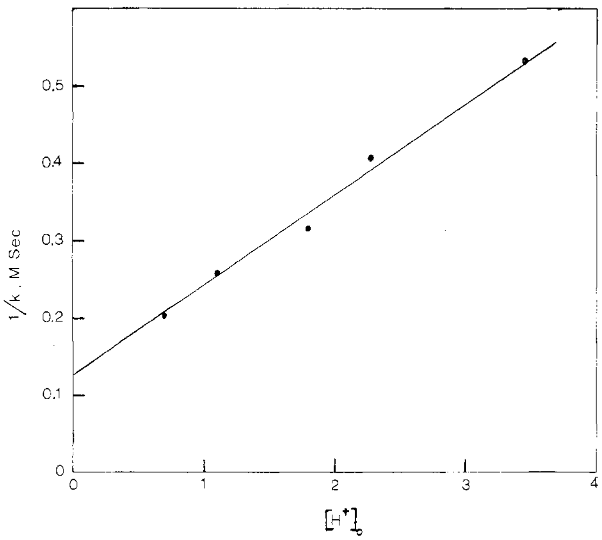

Figure 1. Least-squares plot of eq V.

Assuming appreciable hydrolysis of Ce^{4+} to $CeOH^{3+}$ a rate law of the form

$$-\frac{d[Ce(IV)]}{dt} = k_H[Ce(IV)][CH_3N_2H_4^+] \tag{III}$$

is predicted where

$$k_H = \frac{k_3[H^+] + k_4K}{[H^+] + K} \tag{IV}$$

and K is the first hydrolysis constant of Ce^{4+}. If $k_4K \gg k_3[H^+]$, the reciprocal of eq IV is

$$\frac{1}{k_H} = \frac{[H^+]}{k_4K} + \frac{1}{k_4} \tag{V}$$

A plot of eq V, using the data in Table IV, is shown in Figure 1. It is linear as predicted with a slope ($=1/k_4K$) of 0.119 s and an intercept ($=1/k_4$) of 0.120 M s. The calculated value of K, the hydrolysis constant, is therefore 1.0 M. Hydrolysis constants for Ce^{4+} ranging from $K = 0.2$ to 12 M have been reported. The calculated value of $K = 1.0$ M falls in the middle of this range and is supportive of the proposed rate-determining step.

That $CeOH^{3+}$ is significantly more reactive than Ce^{4+} toward protonated methylhydrazine parallels the relative reactivities of $MnOH^{2+}$ and Mn^{3+} toward hydrazine and its derivatives. In this mechanism one is therefore led to the conclusion that the most important oxidation step is H atom transfer.

The alternative rate-determining step

$$Ce^{4+} + CH_3N_2H_3 \xrightarrow{k_5} Ce^{III} + CH_3N_2H_3\cdot^+ \tag{5}$$

deserves consideration since it also results in the observed relationship between k_H and $[H^+]$,

$$\frac{1}{k_H} = \frac{[H^+]}{k_5K_a} + \frac{K}{k_5K_a} \tag{VI}$$

previously demonstrated by eq V. In eq VI, K is the first hydrolysis constant of Ce^{4+}, and K_a is the ionization constant of $CH_3N_2H_4^+$. Since the observed slope ($=1/k_5K_a$) is 0.119 s, the calculated value of k_5 ($=1/0.119K_a$) is 8.2×10^8 M^{-1} s^{-1}. This was obtained using a value for $K_a = 1.1 \times 10^{-8}$.[10] If step 5 is the rate-determining step then the reaction borders on being diffusion controlled.

Table V. Effect of Aging[a]

Aging time, min	Moles of Ce(IV) × 10^4	Moles of $CH_3N_2H_3$ × 10^4	Ce(IV): $CH_3N_2H_3$	Moles of N_2 × 10^4
9	9.00	55.5	1:6.15	1.90
33	9.00	55.5	1:6.15	1.49
63	9.00	55.5	1:6.15	1.26
91	9.00	55.5	1:6.15	0.981
153	9.00	55.5	1:6.15	0.859
221	9.00	55.5	1:6.15	0.783
266	9.00	55.5	1:6.15	0.719

[a] In all runs the acidity was adjusted to $[HClO_4] = 1.00$ M after aging.

In accordance with the stoichiometric and kinetic results, the $CH_3N_2H_3\cdot^+$ free radical produced in the rate-determining step may be rapidly consumed in two ways. First

$$2CH_3N_2H_3\cdot^+ \rightarrow CH_3N_2H_4^+ + CH_3N_2H: + H^+ \qquad (6)$$

followed by

$$2CH_3N_2H: \rightarrow (CH_3)_2N_2H_2 + N_2 \qquad (7)$$

or second

$$CH_3N_2H_3\cdot^+ + H_2O \rightarrow CH_3OH + N_2 + 4H^+ \qquad (8)$$

where reaction 8 may be a combination of several reactions. The first mechanism yields the overall equation

$$4Ce^{IV} + 2CH_3N_2H_3 \rightarrow 4Ce^{III} + (CH_3)_2N_2H_2 + N_2 + 4H^+ \qquad (9)$$

while the second mechanism yields

$$4Ce^{IV} + CH_3N_2H_3 + H_2O \rightarrow 4Ce^{III} + CH_3OH + N_2 + 4H^+ \qquad (10)$$

Both mechanisms result in the observed N_2:Ce(IV) mole ratio of 1:4. We were not able, however, to further distinguish between the two net reactions.

Effect of Aging. When Ce(IV) was added to water and allowed to age prior to its acidification the amount of N_2 liberated in the reaction was found to decrease severely. For example, after 266 min of aging the N_2 evolution fell to 37% of what was evolved using a freshly prepared acidified Ce(IV) solution. This observation suggests that in an unacidified solution the Ce(IV) undergoes polynuclear complex formation resulting in a different mechanistic pathway. The conditions used in the aging experiments are given in Table V.

Registry No. Ce(IV), 16065-90-0; $CH_3N_2H_3$, 51891-74-8.

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Reduction Potentials of Rare Earth Couples in Liquid Ammonia

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Earlier work revealed the chemical generation of the ammoniated electron via reduction by Yb(II) or Eu(II) in liquid ammonia. Partly to explore this phenomenon further, formal reduction potentials of the Eu(III)/Eu(II) and Yb(III)/Yb(II) couples were determined. This was done by means of potentiometric titrations with AgI or CuI in liquid ammonia at room temperature. An apparatus for high-pressure titration in liquid ammonia at room temperature was developed. The formal reduction potentials for the Eu and Yb couples were found to be 0.063 ± 0.010 and −0.662 ± 0.013 V, respectively. By employing auxiliary data, ΔG° for $Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^-$ was calculated and found to be approximately −71 kJ mol^{-1}. Finally, reduction potentials based on ionic radii and solvation thermodynamics were computed, and these were in satisfactory agreement with the observed values for aqueous systems, but less so for liquid ammonia systems.

Introduction

A principal motivation for the present study was a remarkable reaction observed a few years ago in this laboratory, namely, the production of substantial concentrations of the ammoniated electron by inducing the oxidation of dipositive rare earth ions in liquid ammonia solution.[1] This reaction, $Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^-$, permits preparation of active metals such as potassium by evaporation of the solvent. A similar reaction was observed earlier by Allbut and Fowles,[2] using zirconium(III) salts. In that thermodynamic information on redox reactions can be derived readily from electrometric studies, we undertook the measurement of reduction potentials for the Eu^{3+}/Eu^{2+} and Yb^{3+}/Yb^{2+} couples in liquid ammonia.

The scant information available on electrode potentials in liquid ammonia has been discussed by Jolly[3] and by Jander et al.[4] The known standard reduction potentials are the result of thermodynamic calculations, since a reference electrode of known potential vs. the standard hydrogen electrode has not been available until recently.[5] In no case has the potential of a rare earth couple in liquid ammonia been recorded. The reduction potential of nitrogen ($^1/_2N_2 + 3NH_4^+ + 3e^- \rightarrow 4NH_3$) is very low, only 0.04 V, but fortunately a high overvoltage exists, and a span of approximately 2 V is actually available. Since electrode potentials can be obtained expeditiously from an analysis of titration curves, we devised a pressurized apparatus for carrying out titrations at 25 °C in liquid ammonia medium. Silver or cuprous iodide served as the oxidant. In all earlier apparatus[6] the solutions were cooled to the boiling point of ammonia or below in order to maintain a pressure of 1 atm. Our room-temperature apparatus proved to be simpler and more convenient than the low-temperature assemblies. In the case of the Yb^{3+}/Yb^{2+} couple, an alternative means of constantly varying the ratio of the two ion concentrations was afforded by the known slow oxidation of Yb(II) by NH_4^+.[7]

Experimental Section

Titration Assembly. The apparatus shown in Figure 1 was of stainless steel, except for the buret and rinse-receiving bulb, which