CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE CITY COLLEGE OF THE CITY UNIVERSITY OF NEW YORK, NEW YORK, NEW YORK 10031

Stoichiometry and Kinetics of the Ceric(IV) Oxidation of Hydrazine in Acid Media

BY JACK I. MORROW* AND GARY W. SHEERES

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The oxidation of hydrazine, N_2H_4, by Ce(IV) in acid media was studied. When the mole ratio N_2H_4:Ce(IV) ≥ 3, the stoichiometry of the reaction was found to be constant according to the equation $\mathrm{Ce(IV) + N_2H_5^+ \rightarrow Ce(III) + NH_4^+ + {}^1/_2N_2}$. A detailed kinetic study of this reaction using the stopped-flow technique indicated that $CeOH^{3+}$ oxidizes $N_2H_5^+$ considerably more rapidly than does Ce^{4+}. The reaction at 25° obeys the rate expression $-d[\mathrm{Ce(IV)}]/dt = k_H[\mathrm{Ce(IV)}]\cdot[N_2H_5^+]$. The second-order rate constant, k_H, was found to be hydrogen ion dependent and cerous ion independent. The rate-determining step consistent with our data is

$$\mathrm{CeOH^{3+} + N_2H_5^+ \xrightarrow{k_3} Ce(III) + N_2H_4\cdot^+ + H_2O}$$

Introduction

The oxidation of hydrazine, N_2H_4, by a variety of oxidizing agents has been studied by many workers. Cahn and Powell[1] studied this reaction using iodate, IO_3^-; ferricyanide, $Fe(CN)_6^{3-}$; ceric, Ce(IV); and several other oxidizing agents. They 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. The oxidation of N_2H_4 by molybdenum(VI) was reported on by Huang and Spence.[4] Browne[5] and Bray[6] and their coworkers found three distinct reactions involving one (1), two (2), and four (4) electron changes per mole of hydrazine. Kirk and Browne have speculated on the mechanisms of reactions involving one and two electron oxidations of hydrazine. As early as 1924 Cuy[7] showed that almost invariably the oxidation of N_2H_4 resulted in the evolution of a gaseous product, usually N_2. More recently, Davies and Kustin[8] studied both the stoichiometry and kinetics of the manganic ion (Mn(III)) oxidation of N_2H_4, in perchloric acid solution. They showed that the stoichiometry varied depending upon the relative concentrations of the reactants. More surprising however is that liberation of N_2 was never observed under any set of conditions.

Ce(IV) was chosen as the oxidant in this detailed kinetic study because of its similarity to Mn(III). Both ions undergo one electron reduction and in their oxidation of hydrogen peroxide follow similar mechanisms.[9,10]

The results of this study yield a rate expression for the Ce(IV)–N_2H_4 reaction which is identical in form with that found by Davies and Kustin for the Mn(III)–N_2H_4 reaction but they indicate that a different mechanism is involved since N_2 gas is evolved while the stoichiometry of the reaction is constant.

Experimental Section

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

Fisher Certified reagent grade ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, was used in the preparation of Ce(IV) solutions.

Hydrazine, N_2H_4 (Eastman Organic Chemicals, 64% in H_2O), was used in the preparation of N_2H_4 solutions. It was diluted to approximately 0.4 *M* and analyzed by pH titration with previously standardized HCl solution. This solution was adjusted to the desired concentration and acidity using Baker reagent grade $HClO_4$.

Stoichiometry.—A dual buret gas analyzer apparatus shown in Figure 1 was used to determine the stoichiometry of the reaction. It allows one to mix the two reactants to any desired ratio, then to collect the evolved gas(es) at known pressure and temperature to determine the number of moles liberated, and finally to extract a sample of gas for analysis using the Varian CH 5 mass spectrometer. In use, one of the reactants was pipeted into flask A; the other reactant was contained in buret B. Bulb D was evacuated and then attached to the system using an O-ring ball joint as shown in Figure 1. With stopcocks 3 and 4 open and stopcock 1 closed, helium was then allowed to flow through stopcock 2 into flask A and the entire system (except for bulb D) to purge it of air and replace it with helium at atmospheric pressure. After purging, stopcock 4 was turned to permit the gas buret (G) to communicate with flask A, and stopcocks 2 and 3 were closed. The helium was then adjusted to atmospheric pressure by matching the heights of liquid in gas buret G and in the leveling bulb, H. The contents of buret B were then admitted into flask A through stopcock 1. If no gas(es) was evolved, then the volume of liquid entering flask A would displace an equivalent volume of gas back into buret B and the liquid level in gas buret G would remain unchanged. The liquid level in buret G would change only if gas was evolved in the reaction. In this manner, the volume of gas liberated at constant temperature and pressure was determined. After the volume of liberated gas was determined, stopcock 4 was closed off, and stopcock 2 opened thereby permitting extraction of a sample of gas from flask A into bulb D. Stopcock 2 was then closed. In this manner a sample of the product gas(es) was then obtained for mass spectrometric analysis.

Kinetic Measurements.—Rates of reaction were followed by measuring the decrease in absorbance of Ce(IV) at 290 nm using the Aminco-Morrow stopped-flow apparatus[11] attached to an Aminco monochromator. The detector used was an R-136 photomultiplier (PMT) powered by a Harrison 6515A dc power supply. The PMT output was fed into the Aminco linear-log kinetic photometer and the logarithmic (absorbance) signal was then displayed using the Tektronix 564B storage oscilloscope. Figure 2 shows a typical oscilloscopic trace of the reaction.

Results and Discussion

Table I gives the results of the stoichiometry determination when the quantity of hydrazine was in excess over that of Ce(IV). This is analogous to the conditions used in kinetic runs. Under these conditions

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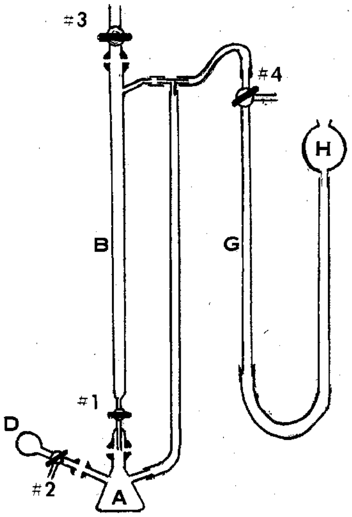

Figure 1.—Dual buret gas analysis apparatus.

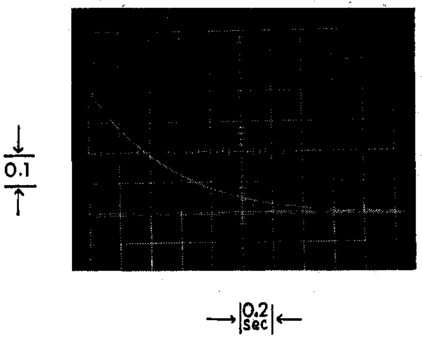

Figure 2.—Typical kinetic trace using stopped-flow apparatus. This particular trace corresponds to experiment number 6 in Table II.

TABLE I

N_2:Ce(IV) MOLE RATIO[a]

Expt no.	Amt × 10^4, mol		Mole ratio[b]
	Ce(IV)	N_2H_4	N_2:Ce(IV)
1	3.00	26.9	1:2.08
2	2.00	18.0	1:2.06
3	0.500	4.49	1:2.15

[a] All runs were performed at 25°. The ($HClO_4$) = 1 *M* in all solutions. In experiment no. 1, 3 ml of 0.100 *M* Ce(IV) solution was mixed with 30 ml of 0.0898 *M* N_2H_4; in experiment no. 2, 2 ml of 0.100 *M* Ce(IV) was mixed with 60 ml of 0.0299 *M* N_2H_4; in experiment no. 3, 5 ml of 0.0100 *M* Ce(IV) was mixed with 50 ml of 0.00898 *M* N_2H_4. [b] Reported values are the average of three replicate runs. The values were reproducible to within ±2%.

a mole ratio of N_2:Ce(IV) of 1:2 was obtained consistent with the reaction

$$\mathrm{Ce(IV)} + N_2H_4 \longrightarrow \mathrm{Ce(III)} + {}^1/_2N_2 + NH_4^+ \qquad (1)$$

Although hydrazine is written in reaction 1 as N_2H_4, it is a basic molecule and exists primarily as $N_2H_5^+$ in acid solution.

When the Ce(IV) was placed in excess over the N_2H_4, the N_2:N_2H_4 mole ratio attained a value of 1:1 and was reproducible to within ±5% for Ce(IV):N_2H_4 mole ratios of 15:1 to 3:1. In these runs the N_2H_4 solution was added to the Ce(IV) solution. For the same mole ratio of reactants, but reversing the order of addition, the mole ratio of N_2:N_2H_4 was about 1.7. These data indicate that with Ce(IV) in excess, the hydroxyl free radical produced in the rate-determining steps 2 and 3 (discussed later) probably undergoes a second oxidation by the Ce(IV) resulting in a different stoichiometry. When the N_2H_4:Ce(IV) mole ratio was 3:1 and greater, the N_2:Ce(IV) mole ratio was constant at 1:2 and was independent of the order of addition. This constancy was observed for N_2H_4:Ce(IV) mole ratios of 3:1, 5:1, and 9:1 (see Table I). It seems reasonable to expect that this constancy would be maintained at the kinetic conditions where the mole ratio, N_2H_4:Ce(IV) > 100:1.

The two electron oxidation of N_2H_4 will not be discussed further since at our experimental kinetic conditions, the one electron oxidation leading to the mole ratio data presented in Table I dominates.

Table II contains first-order rate constants, k_{obsd}, defined (at constant $[H^+]_0$ and $[N_2H_5^+]_0$) by eq I.

TABLE II[a]

Expt no.[a]	10^4·[Ce(IV)]$_0$, *M*	10^2·[N_2H_4]$_0$, *M*	10^2[Ce(III)], *M*	k_{obsd},[b] $\sec^{-1}$	k_H, $M^{-1}\sec^{-1}$
1	1.00	10.1	0.00	1.00	9.9
2	2.00	10.1	0.00	0.94	9.3
3	4.00	10.1	0.00	0.94	9.3
4	4.00	5.06	0.00	0.48	9.5
5	4.00	19.9	0.00	2.04	10.2
6	4.00	29.8	0.00	3.15	10.5
7	4.00	5.06	0.50	0.43	8.5
8	4.00	5.06	1.00	0.50	9.9
9	4.00	5.06	2.50	0.46	9.1
10	4.00	5.06	5.00	0.50[c]	9.9
11	4.00	5.06	10.00	0.55[c]	10.8

[a] In all experiments ($HClO_4$) = 1.0 *M*. [b] Each value of k_{obsd} is the result of at least three replicate runs. The agreement between replicate runs was within ±2%. [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 concentrations used in these runs was appreciable at 290 nm.

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = k_{\text{obsd}}[\mathrm{Ce(IV)}] \qquad (I)$$

The second-order rate constant, k_H, defined by eq II

$$k_H = \frac{k_{\text{obsd}}}{[N_2H_5^+]_0} \qquad (II)$$

was constant at 9.6 ± 0.5 $M^{-1}\sec^{-1}$. This second-order rate constant was found to be cerous ion independent but was dependent upon the acidity.

Hydrogen Ion Dependency and Mechanism.—Table III gives the effect of acidity upon k_H. These results are readily interpreted if the assumption is made that all protolytic steps are rapid with respect to reactions 2 and 3 which are rate determining. Both of these re-

TABLE III

VARIATION OF k_H WITH ACIDITY

Expt no.	10^4[Ce(IV)], *M*	10^2(N_2H_4), *M*	($HClO_4$), *M*	k_H,[a] $M^{-1}\sec^{-1}$
1	4.00	5.15	0.50	14.2
2	4.00	5.15	1.00	8.4
3	4.00	5.15	2.00	3.5
4	4.00	5.15	3.00	2.4

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

$$Ce^{4+} + N_2H_5^+ \xrightarrow{k_2} Ce^{3+} + N_2H_4\cdot^+ + H^+ \qquad (2)$$

$$CeOH^{3+} + N_2H_5^+ \xrightarrow{k_3} Ce^{3+} + N_2H_4\cdot^+ + H_2O \qquad (3)$$

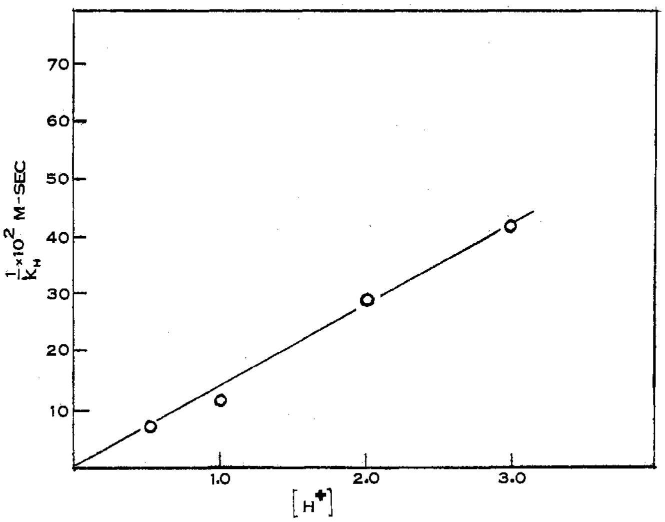

Figure 3.—Plot of $1/k_H$ *vs.* (H^+).

actions produce the $N_2H_3\cdot$ free radical which in acid solution is believed to be protonated[12,13] $(N_2H_4\cdot{}^+)$.

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

$$-\frac{d[Ce(IV)]}{dt} = k_H[Ce(IV)][N_2H_5^+] \qquad (III)$$

is predicted where

$$k_H = \frac{k_2(H^+) + k_3K}{(H^+) + K} \qquad (IV)$$

and K $(= [(CeOH^{3+})(H^+)]/(Ce^{4+}))$ is the first hydrolysis constant of Ce^{4+}. If $k_3K \gg k_2(H^+)$, the reciprocal of eq IV is

$$\frac{1}{k_H} = \frac{(H^+)}{k_3K} + \frac{1}{k_3} \qquad (V)$$

A plot of eq V is shown in Figure 3. It is linear as predicted with a slope $(=1/k_3K)$ of 0.15 sec. Baker, Newton, and Kahn[14] have estimated that in 2 M $HClO_4$ the first hydrolysis of Ce^{4+} is at least 85% complete. This would indicate that the first hydrolysis constant is $K \approx 12$ M. Offner and Skoog[15] also studied this hydrolysis and reported a value of $K \approx 0.2$ M. Because of the significant difference between these reported hydrolysis constants, calculating the value of k_3 from the slope of Figure 3 would be meaningless. It is, however, obvious that k_3 is much greater than k_2.

That $CeOH^+$ is so much more reactive than Ce^{4+} toward protonated hydrazine molecules is similar to Davies and Kustin's[8] observation regarding the relative reactivity of $MnOH^{2+}$ and Mn^{3+} toward $N_2H_5^+$. We are therefore also led to the conclusion that the most important oxidation mechanism is H atom transfer. The ultimate fate, however, of the protonated hydrazyl free radical is necessarily different when Ce(IV) rather than Mn(III) is used as the oxidant since N_2 gas is formed in the former case and not in the latter case. In this study, with Ce(IV) as oxidant the hydrazine probably follows the one electron oxidation scheme proposed by Kirk and Browne and discussed by Cahn and Powell[1]

$$N_2H_4 \longrightarrow N_2H_3 \longrightarrow NH_2NHNHNH_2 \longrightarrow 2NH_3 + N_2$$

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BRIGHAM YOUNG UNIVERSITY, PROVO, UTAH 84601

High-Pressure Synthesis of Rare Earth Dimanganese Compounds with the $MgZn_2$ (Laves) Structure[1]

BY NORMAN L. EATOUGH*[2] AND H. TRACY HALL

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Laves structures of the $MgZn_2$ type were synthesized for $GdMn_2$, $TbMn_2$, $DyMn_2$, $HoMn_2$, YMn_2, and $YbMn_2$ under high-temperature and high-pressure conditions. All but the Yb compound were previously known only in the $MgCu_2$ structure. $YbMn_2$ had not been prepared before this work. Also the synthesis of $ErMn_2$ was verified and $SmMn_2$ was prepared at high pressure.

Introduction

The rare earth dimanganese ($REMn_2$) compounds are known to exhibit some interesting changes in crystal structure as the atomic number of the rare earth varies.[3] Both the light and heavy rare earths (at 1 atm) form $REMn_2$ compounds in the C14 ($MgZn_2$) Laves structure while the intermediate rare earths form $REMn_2$ compounds in the C15 ($MgCu_2$) Laves structure. This information is summarized in Table I as are, also, the high-pressure results of this paper.

[1] This research supported by the U. S. Army Research Office-Durham and the National Science Foundation.

[2] Author to whom correspondence should be addressed at the California State Polytechnic College, San Luis Obispo, California.

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