Reduction of Dodecatungstocobaltate(III) by Aqueous Solutions of Hydrazinium Ion

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Abstract

The kinetics of the reduction of dodecatungstocobaltate(III) anion by hydrazinium ion has been studied in aqueous hydrochloric acid. The data are consistent with the rate law

$$-d\,\frac{[\text{oxidant}]}{dt} = k_2\,[\text{oxidant}]\,[\text{reductant}]$$

with $k_2 = (1.80 \pm 0.05) \times 10^{-2}$ mol^{-1} dm^3 S^{-1}, $\Delta H^{\ddagger} = 46.7 \pm 0.8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -121 \pm 5$ J K^{-1} mol^{-1} at $I = 2.0$ mol dm^{-3} (NaCl), [H$^+$] = 0.1– 1.5 mol dm^{-3} and $T = 24.5\ ^\circ$C. Added copper(II) ions catalysed the rate and the reduction is interpreted in terms of the outer-sphere mechanism.

Introduction

Several reports of the kinetics of oxidation of hydrazine and hydrazinium ion by metal ion complexes have been made [1–9]. Except in a few cases [3, 4, 7], spectrophotometric and kinetic evidence has been used to show that the reactions occur via intermediates with inner-sphere character. By contrast, our experience [10–15] and those of others [16–19] suggest that because of the substitution inertness of dodecatungstocobaltate(III) anion, its reactions are best interpreted in terms of the outer-sphere mechanism. As part of our interest in the dynamics of dodecatungstocobaltate reactions, we now report the results of the investigation of the stoicheiometry, intermediates and kinetics of the titled reaction in the hope of relating our findings to the points raised above. For convenience, dodecatungstocobaltate(III) anion and its divalent counterpart, dodecatungstocobaltate(II) anion, will be designated Co^{III}W$_{12}$ and Co^{II}W$_{12}$ subsequently.

Experimental

Materials

Potassium dodecatungstocobaltate(III) was prepared and standardized as described previously [10]. Stock solutions of hydrozinium ion were freshly prepared by dissolving known quantities of hydrazine monohydrochloride (Aldrich) in doubly distilled water and the solutions were standardized by the acid bromate method [20]. Hydrochloric acid was employed to vary the hydrogen ion concentration while sodium chloride was used as supporting electrolyte. Fresh stock solutions of CuCl$_2$ (B.D.H. Analar) were prepared and standardized; and these were used to prepare Cu^{2+}(aq) solutions for kinetic runs. All other chemicals were used as received.

Stoicheiometric Studies

Stoicheiometric studies were carried out in an excess of hydrazinium ion. Five reaction mixtures containing [Co^{III}W$_{12}$]$_0$ = (1–5) × 10^{-3} mol dm^{-3}, [N$_2$H$_5^+$]$_0$ = (2.5–10.0) × 10^{-3} mol dm^{-3} at [H$^+$]$_0$ = 0.5 mol dm^{-3} and I = 2.0 mol dm^{-3} were allowed to stand in 10 cm^3 flasks. After 24 h, the unconsumed hydrazinium ion was determined by potassium bromate [20].
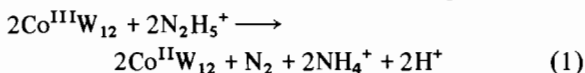
Kinetics

The kinetics of the reactions were studied by following the decrease in the absorbance Co^{III}W$_{12}$ at 388 nm (ϵ = 1150 ± 5 mol^{-1} dm^3 cm^{-1} [16]) using a Pye-Unicam SP 1750 spectrophotometer fitted with thermostated cell holders. All kinetic runs were preformed under pseudo-first-order conditions with the concentrations of hydrazinium ion in a large excess over those of Co^{III}W$_{12}$. Unless otherwise indicated, all kinetic studies were conducted at an ionic strength of 2 mol dm^{-3} maintained by the addition of sodium chloride.

Results and Discussion

Stoicheiometry

The results of stoicheiometric studies displayed in Table 1, suggest that with N$_2$H$_5^+$ in excess, the overall reaction may be represented by eqn. (1).

$$2\text{Co}^{III}\text{W}_{12} + 2\text{N}_2\text{H}_5^+ \longrightarrow$$
$$2\text{Co}^{II}\text{W}_{12} + \text{N}_2 + 2\text{NH}_4^+ + 2\text{H}^+ \qquad (1)$$

The formation of Co^{II}W$_{12}$ in reaction (1) was confirmed by the appearance of its characteristics absorption peak at 625 nm [16].

TABLE 1. Stoichiometry of the reaction of dodecatungsto-cobaltate(III) anion with hydrazinium ion

$Co^{III}W_{12}$ (mmol)	$N_2H_5^+$ (mmol)	$(N_2H_5^+)$ (mmol)	$(Co^{III}W_{12})/$ $(N_2H_5^+)$
1.00	2.50	1.04	0.96
1.75	4.00	1.80	0.97
3.00	6.85	2.91	1.03
4.00	8.50	4.08	0.98
5.00	10.00	4.90	1.02

Studies of the stoicheiometries of the oxidation of hydrazine and substituted hydrazines do not always give definitive results. For example the ratio n(Δ oxidant/Δ reductant) for the reaction of $IrCl_6^{3-}$ and hydrazine has been reported by some investigators to be 4 [21] when $IrCl_6^{3-}$ was in excess and 4 [3] or 1 [22] when hydrazine was in excess. Various values of n have also been quoted for the analogous reaction of other one-electron oxidants, e.g. Mn^{III}-(Cdta)H_2O (Cdta = transcyclohexane-1,2-diamine-N,N,N',N'-tetracetate), n = 1 [5]; $Fe(CN)_6^{3-}$, n = 4 [8] and $Mo(CN)_8^{3-}$ n = c. 5 [8]. Since the kinetic studies were conducted under pseudo-first-order conditions with hydrazinium ion in a large excess ($n \ll 1$), 1:1 reaction stoicheiometry is probably maintained throughout the present study.

Spectrophotometric Test for Intermediate Complex

The electronic spectra of solutions containing $Co^{III}W_{12}$ (1–5 $\times$ 10^{-4} mol dm^{-3}) in [H$^+$] = 0.10–1.00 mol dm^{-3} and those containing mixtures of $Co^{III}W_{12}$ (2 $\times$ 10^{-4} mol dm^{-3}), [$N_2H_5^+$]$_0$ = 0.01–0.10 mol dm^{-3} in 0.01 $\leqslant$ [H$^+$] $\leqslant$ 1.00 mol dm^{-3} at I = 2.0 mol dm^{-3} (NaCl) were compared between 330 and 500 nm. There was no clear shift in the λ_{max} or ϵ value of $Co^{III}W_{12}$. Although this does not completely negate the formation of an intermediate complex, it suggests that the intermediate complex (if any) must have a very small formation constant.

Test for Free Radicals

The hydrazyl free radical, $N_2H_4^{+\cdot}$ is a well established intermediate in the oxidation of hydrazines. Its presence has been confirmed by a variety of techniques ranging from pulse radiolysis [23], reduction with Cu^{2+} [24], ESR spectroscopy [25] to polymerization studies [2]. In the present study, due to the absence of equipment for other techniques, the polymerization test and reduction with Cu^{2+} were employed. The polymerization test was carried out at [H$^+$] = 0.50 mol dm^{-3} by the addition of 5.0 cm^3 of 30% (wt./vol) acrylamide to 1.0 cm^3 of 5.0 mol dm^{-3} $N_2H_5^+$ and 2.0 cm^3 of 2 $\times$ 10^{-3} mol dm^{-3} $Co^{III}W_{12}$ stock solutions. The total volume was adjusted to 10 cm^3 and the formation of poly-

acrylamide was noticed by adding a large excess of methanol. Since blank experiments from which either $Co^{III}W_{12}$ or $N_2H_5^+$ was excluded gave no detectable polymers, it appears free radicals, possibly the protonated hydrazyl radical, $N_2H_4^{+\cdot}$ is produced in the reaction. (Discussion of the effect of Cu^{2+} on the rate of reaction is deferred.).

Kinetics and Mechanism

When the concentration of hydrazinium ion is in at least fifty fold excess over that of $Co^{III}W_{12}$, plots of log($A_t - A_\infty$) (A_t and A_∞ are respectively the absorbances at times t and at the end of reaction) versus time were linear in more than 80% of the reactions. From the slopes of such linear plots, the pseudo-first-order rate constants, k_{obs}, were determined at different initial concentrations of $N_2H_5^+$, $Co^{III}W_{12}$, and hydrogen ions. Representative kinetic data are displayed in Table 2. The linearity of pseudo-first-order plots and the invariance of k_{obs} with different initial concentrations of $[Co^{III}W_{12}]_0$ indicate that the reaction is first-order with respect to the oxidant.

Values of k_{obs} were found to be independent of hydrogen ion concentrations in the 0.10–1.50 mol dm^{-3} range. This suggests that partition between protonation levels is negligible in the acidity range investigated. Since the pK_a of hydrazinium ion is c. 8.0 [2] and most of the kinetic studies were conducted at [H$^+$] = 0.50 mol dm^{-3}, it appears that the protonated substrate, $N_2H_5^+$ is the dominant species of the reductant under the experimental conditions. Nevertheless, the existence of some $N_2H_6^{2+}$ which has pK_a = 11.2 mol dm^{-3} [1] cannot be ruled out.

Plots of k_{obs} against [$N_2H_5^+$] display the first-order dependence of rate on the concentration of $N_2H_5^+$ at different temperatures. The intercept obtained in each case by the method of least-squares is insignificant, showing lack of appreciable kinetic evidence for other oxidation pathways. Thus, at a constant [H$^+$] and temperature, the rate equation for the reaction is

$$-d\frac{[Co^{III}W_{12}]}{dt} = k_2[Co^{III}W_{12}][N_2H_5^+] \qquad (2)$$

Values of the second-order rate constant, k_2, obtained at four different temperatures, together with the activation parameters determined from a least-squares analysis of plots of log k_2/T versus $1/T$ are reported in Table 3.

The reaction was also investigated in the presence of different salts, such as sodium chloride, lithium chloride, potassium chloride and sodium perchlorate. The results in Table 4 indicate that anions have little effect on the pseudo-first-order rate constants while cations markedly affect the rate constants. It therefore seems that cations play a catalytic role, which

TABLE 2. Pseudo-first-order rate of oxidation of $N_2H_5^+$ by $Co^{III}W_{12}$ at $X = 388$ nm and $I = 2.0$ mol dm^{-3} (NaCl)

T (°C)	$10^4 \times [CoIIIW_{12}]$ (mol dm^{-3})	$[N_2H_5^+]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	$10^3 \times k_{obs}$ (s^{-1})
29.8	2.00	0.01	1.50	0.29
	2.00	0.03	0.50	0.79
	2.00	0.04	0.10	1.09
	2.00	0.06	1.00	1.63
	2.00	0.08	0.50	2.16
$k_2 = (2.69 \pm 0.13) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}				
24.5	1.00	0.01	0.50	0.19
	2.00	0.01	0.50	0.18
	4.00	0.01	0.50	0.20
	5.00	0.01	0.50	0.19
	2.00	0.03	0.50	0.55
	2.00	0.05	0.50	0.90
	2.00	0.05	0.05	0.90
	2.00	0.07	0.50	1.28
	2.00	0.08	0.50	1.45
	2.00	0.10	0.50	1.81
	2.00	0.05	0.10	0.88
	2.00	0.05	0.75	0.90
	2.00	0.05	1.00	0.92
	2.00	0.05	1.50	0.89
$k_2 = (1.80 \pm 0.05) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}				
20.4	2.00	0.02	0.50	0.30
	2.00	0.04	1.00	0.58
	2.00	0.06	0.10	0.86
	2.00	0.08	0.50	1.16
	2.00	0.10	1.50	1.45
$k_2 = (1.44 \pm 0.05) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}				
14.6	2.00	0.02	0.10	0.19
	2.00	0.04	0.50	0.37
	2.00	0.06	0.50	0.55
	2.00	0.08	1.50	0.73
	2.00	0.10	0.50	0.91
	2.00	0.12	0.50	1.10
$k_2 = (0.91 \pm 0.02) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}				

TABLE 3. Effect of Cu^{2+} on the pseudo-first-order rate at 29.8 °C

$10^5 \times [Cu^{2+}]$ (mol dm^{-3})	0	0.5	0.8	1.0	2.0	2.5
$10^3 \times k_{obs}$ (s^{-1})	2.16	5.99	7.46	9.45	15.26	20.26

$k_{Cu}2+ = (6.98 \pm 0.76) \times 10^2$ mol^{-2} dm^6 s^{-1}

TABLE 4. Apparent first-order rate constants in different media at 24.5 °C, $[N_2H_5^+] = 0.5$ mol dm^{-3}, $[H^+] = 0.50$ mol dm^{-3}, $[Co^{III}W_{12}] = 2.00 \times 10^{-4}$ mol dm^{-3} and $I = 2.0$ mol dm^{-3} (B)

Medium (B)	LiCl	NaCl	NaClO$_4$	KCl
$10^3 \times k_{obs}$ (s^{-1})	0.35	0.55	0.58	1.82

increases in the sequence $Li^+ < Na^+ < K^+$. Similar observations have already been reported [15, 16, 18, 19]. This increase in rate constant with increasing size of the cation is in keeping with the fact that larger ions lead to larger ion-pairing with this anionic oxidant. Alternatively, the large increase in the reaction rates may be due to the greater effectiveness of the larger cations (due to their larger polarizabil-

ities) to act as better bridges for electron transfer. Distinction between these two factors cannot be made unequivocally from our present results.

From the results discussed above, it appears that the mechanism of the titled reaction may be formulated as shown below.

$$Co^{III}W_{12} + N_2H_5^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co^{II}W_{12} + H^+ + \dot{N}_2H_4^+ \qquad (3)$$

$$2(\dot{N}_2H_4^+) \overset{k_3}{\longrightarrow} N_2 + 2NH_4^+ \qquad (4)$$
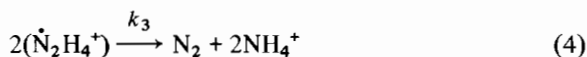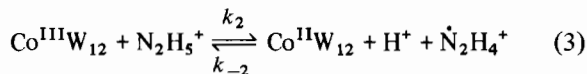
The first step involves electron transfer from $N_2H_5^+$ to $Co^{III}W_{12}$ to give $Co^{II}W_{12}$ and the protonated hydrazyl radical cation $\dot{N}_2H_4^+$. The radical is then lost through disproportionation rather than by further reaction with another molecule of the oxidant. Such a mechanism is analogous to that proposed for the reaction of NH_3OH^+ with $Co^{III}W_{12}$, in keeping with the suggestion that $N_2H_5^+$ and NH_3OH^+ react via similar mechanisms with the same oxidants [5].

Added Cu^{2+}, varied between $(0.5–2.5) \times 10^{-5}$ mol dm^{-3} at constant $Co^{III}W_{12}$, $[H^+]$, $[N_2H_5^+]$, and $I = 2.0$ mol dm^{-3} (NaCl) at $T = 29.8$ °C, catalysed the rate of reaction (Table 5) and a plot ($r = 0.9967$) of the apparent rate constant k_{obs} against $[Cu^{2+}]$ fitted eqn. (5)

$$k_{obs} = k_0 + k_{Cu^{2+}}[Cu^{2+}] \qquad (5)$$

where k_0 and $k_{Cu^{2+}}$ are the rate constants for the uncatalysed and catalysed reactions, respectively. Under the conditions quoted above, $k_0 = (2.19 \pm 0.05) \times 10^{-3}$ s^{-1} and $k_{Cu^{2+}} = (6.98 \pm 0.12) \times 10^2$ mol^{-1} dm^3 s^{-1}. The catalytic effect of added Cu^{2+} in reactions of hydrazine suggest that the hydrazyl radical cation, $\dot{N}_2H_4^+$ is an intermediate in the reactions and that the analogue of reaction (3) is reversible [24]. Thus, the observed Cu^{2+} catalysis tends to corroborate the occurrence of the proposed mechanism in the absence of added Cu^{2+}. If the steady state approximation is applied to reactions (3) and (4), the rate of loss of $Co^{III}W_{12}$ may be expressed by eqn. (6)

TABLE 5. Second order rate constants k_2 for the reaction of $Co^{III}W_{12}$ and $N_2H_5^+$ at different temperatures

T (°C)	$10^2 \times k_2{}^a$ (mol^{-1} dm^3 s^{-1})
14.6	0.91 ± 0.02
20.4	1.44 ± 0.05
24.5	1.80 ± 0.05
29.8	2.69 ± 0.13
$\Delta H^{\ddagger} = 46.7 \pm 0.8$ kJ mol^{-1}	
$\Delta S^{\ddagger} = 121 \pm 5$ J K^{-1} mol^{-1}	

aError expressed as standard deviation.

$$-d \frac{[Co^{III}W_{12}]}{dt} = \frac{k_2 k_3 [Co^{III}W_{12}]^2 [N_2H_5^+]}{k_{-2}[Co^{III}W_{12}][H^+] + k_3[Co^{III}W_{12}]} \qquad (6)$$

Provided $k_3[Co^{III}W_{12}] \geqslant k_{-2}[Co^{III}W_{12}][H^+]$, eqn. (6) leads to the empirical rate law depicted by eqn. (2). Under the experimental conditions employed in this study, k_2 was evaluated to be $(1.81 \pm 0.18) \times 10^{-1}$ mol^{-1} dm^3 s^{-1} at 24.5 ± 0.1 °C.

Many oxidations of hydrazine and hydrazine derivatives by metal ion complexes occur via intermediate complexes [6], which possess inner-sphere character. However, the cobalt(III) ion in dodecatungstocobaltate(III) anion is tetrahedrally surrounded by four oxygen atoms and this tetrahedral is in turn coordinated to four W_3O_{13} octahedra, which are retained on redox [26]. Therefore any intermediate formed between the oxidant and the reductant would be expected to be weak. In keeping with this, there is no spectrophotometric or kinetic evidence for an intermediate complex in this study.

Since information on outer-sphere oxidation of hydrazine is scanty, an attempt was made to interprete our results in terms of the correlations predicted by Marcus [27] and Schuster [28]. Marcus [27] predicted that for an outer-sphere reaction

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \qquad (7)$$

$$\log k_{12} = 0.5(\log k_{11} + \log k_{22} + \log f) + 8.46n(\Delta E^\circ) \qquad (8)$$

where k_{12} is the cross-reaction rate constant, k_{11} and k_{22} are self-exchange rate constants, and K_{12} is the equilibrium constant. Thus it is expected that a plot of $\log k_{12}$ versus E° for such a reaction would be linear with a slope of 8.46 V^{-1} at 25 °C [27]. But Schuster [28] predicted the slope of this line to be -16.9 V^{-1} when the electron transfer step is rate-determining.

Table 6 includes the values of the terms required to correlate the rate constant with the driving force for the oxidation of hydrazine by $Co^{III}W_{12}$, $IrCl_6^{2-}$ [3] and $Ni(dmg)_3^{2-}$ [4]. These data gave a reasonably linear plot ($r = 0.8982$) with a slope of -12.97 V^{-1}, which is qualitatively consistent with that predicted by Schuster [28]. However, any conclusion based on the plot must be accepted with some reservations in view of the scarcity of data and precision with which the various parameters used are known.

It appears that the substitution inertness of the oxidant [26] as well as the absence of spectrophotometric or kinetic evidence for intermediate complex and the dependency of k_2 on the driving force E° of the reaction show that the outer-sphere

TABLE 6. Kinetic and thermodynamic parameters for the oxidation of hydrazine by some one electron oxidants at 25 °C

Oxidant	k_2 (mol^{-1} dm^3 s^{-1})	Reduction potential (V)	Reference
Co^{III}W$_{12}$	1.89×10^{-2}[a]	1.00	this work
IrCl$_6{}^{2-}$	5.03×10^3	0.89	3
Ni(dmg)$_3{}^{2-}$	2.85×10^7[b]	0.40	4

[a]Estimated from the data obtained at 24.5 °C.   [b]Extrapolated from the data at 35 °C.

pathway has an advantage over the inner-sphere path for the titled reaction. In this respect, the reaction is similar to the corresponding rate-determing reductions of the oxidant by a wide range of substrates [10—18].

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