Inorganica Chimica Acta, 50 (1981) 251–255
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Osmium Tetroxide Reduction with Thiourea in Perchloric Acid Solutions

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Received October 29, 1980

The reduction of OsO_4 by means of thiourea has been extensively studied both in $H_2O/EtOH$ and H_2O in presence of $HClO_4$. The kinetic experiments were carried out spectrophotometrically in time-drive, in pseudo-first order conditions of the perchloric acid and thiourea concentrations with respect to OsO_4, keeping constant the ionic strength. The reaction rate depends on the first power of $|OsO_4|$. The pseudo-first order k_{obs}s are linear with thiourea concentrations in both media, but they are linear with $|HClO_4|$ in $H_2O/EtOH$ and show a more complicate dependence on the acid in pure H_2O. The specific rate constants of the significant kinetic processes have been evaluated together with their activation parameters.

Introduction

The reaction between OsO_4 and thiourea (tu) in acidic $H_2O/EtOH$ medium is used for the quantitative determination of osmium [1, 2]. In fact, this reaction yields a red complex of Os(III), *i.e.* $[Os(tu)_6]^{3+}$, whose concentration can easily be determined by spectrophotometric measurements. Recently [3], a preliminary kinetic study on this reaction has been reported. The aim of that investigation was to compare the reactivity of several N,N′-substituted thioureas towards OsO_4. There, the influence of the perchloric acid concentration and of the dielectric constant on the observed rate constants (k_{obs}) was pointed out. On the basis of the plots of k_{obs} *versus* $|HClO_4|$, a rate equation of the type

$$v = (k'|HClO_4| + k'')|OsO_4| \qquad (1)$$

was hypothesized for all the considered thioureas, although the k'' value for tu was very close to zero. In those experiments, the concentration of thioureas was kept constant, always in pseudo-order condition with respect to the substrate.

Now, we have extended the study of reduction of Os(VIII) by tu, in order to obtain more details on the reaction mechanism.

Results and Discussion

All the kinetic measurements were performed in large excess of perchloric acid and thiourea concentrations in order to assure the pseudo order conditions with respect to the osmium. The ionic strength was kept constant by means of sodium perchlorate. The kinetics were followed spectrophotometrically by measuring the absorbance of the complex during its formation until the end reaction was reached. The final value of the absorbance (A_∞) decreases in time; however, the rate of this decomposition is much slower than that of the complex formation and, consequently, it does not affect the kinetic measurements.

By plotting $\ln(A_\infty - A_t)$ *versus* time, straight lines are obtained, whose slopes are the k_{obs}s. The pseudo-first order rate constants, obtained by carrying out the reaction in $H_2O/EtOH$ (1:1 vol) with different amounts of $HClO_4$ and tu at various temperatures, are listed in Table I.

The k_{obs}s, plotted both against $|HClO_4|$ and against $|tu|$, give straight lines, which cross the origin in the case of the plot $k_{obs}/|HClO_4|$, while they show positive intercepts for $k_{obs}/|tu|$. A typical pattern of $k_{obs}/|HClO_4|$ at different concentrations of tu is pictured on the left hand of Fig. 1. This means that

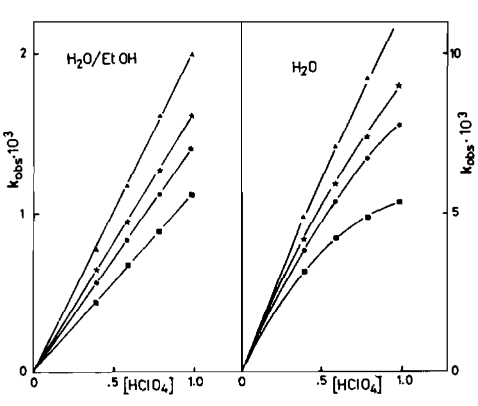

Fig. 1. Plots of k_{obs} *versus* $|HClO_4|$ in $H_2O/EtOH$ and H_2O at 20 °C, at different thiourea concentrations ([tu]: ▲ = 1.41×10^{-2}, ★ = 1.06×10^{-2}, ● = 0.88×10^{-2} and ■ = 0.53×10^{-2}); $\mu = 0.981$.

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TABLE I. Pseudo-first Order Rate Constants ($k_{obs} \times 10^3$) for the Reduction of OsO_4 by Thiourea in H_2O/EtOH (1:1 vol); μ = 0.981.

$\|HClO_4\|$	$\|tu\| \times 10^2$	t °C			
		20	30	37	45
0.981	1.41	1.98 ± 0.02	4.70 ± 0.03	7.79 ± 0.07	14.69 ± 0.07
	1.06	1.62 ± 0.05	3.96 ± 0.02	6.53 ± 0.15	12.65 ± 0.12
	0.88	1.41 ± 0.05	3.48 ± 0.02	6.29 ± 0.05	11.62 ± 0.02
	0.53	1.12 ± 0.02	2.70 ± 0.02	4.84 ± 0.03	9.40 ± 0.03
0.785	1.41	1.61 ± 0.01	3.59 ± 0.02	6.06 ± 0.09	11.64 ± 0.06
	1.06	1.26 ± 0.01	3.16 ± 0.09	5.31 ± 0.06	9.87 ± 0.10
	0.88	1.13 ± 0.01	2.65 ± 0.01	4.86 ± 0.03	9.10 ± 0.10
	0.53	0.89 ± 0.01	2.08 ± 0.03	3.81 ± 0.06	7.74 ± 0.03
0.588	1.41	1.17 ± 0.01	2.58 ± 0.02	4.51 ± 0.12	8.18 ± 0.10
	1.06	0.94 ± 0.01	2.28 ± 0.09	3.91 ± 0.05	7.07 ± 0.07
	0.88	0.83 ± 0.01	2.03 ± 0.01	3.48 ± 0.05	6.73 ± 0.11
	0.53	0.66 ± 0.01	1.51 ± 0.02	2.93 ± 0.03	5.84 ± 0.06
0.392	1.41	0.77 ± 0.01	1.81 ± 0.02	2.83 ± 0.03	5.50 ± 0.04
	1.06	0.64 ± 0.01	1.52 ± 0.12	2.67 ± 0.05	4.90 ± 0.06
	0.88	0.57 ± 0.01	1.31 ± 0.02	2.34 ± 0.03	4.62 ± 0.06
	0.53	0.44 ± 0.01	1.06 ± 0.01	2.01 ± 0.02	3.88 ± 0.05

TABLE II. k_1 and k_2 Specific Rates and Activation Parameters for the Reaction in H_2O/EtOH (1:1 vol).

t (°C)	$k_1 \times 10$ ($mol^{-2}\,l^2\,sec^{-1}$)	$k_2 \times 10^3$ ($mol^{-1}\,l\,sec^{-1}$)	r^a
20	1.02 ± 0.05	0.58 ± 0.05	0.997
30	2.30 ± 0.11	1.52 ± 0.11	0.998
37	3.54 ± 0.26	3.07 ± 0.26	0.995
45	6.06 ± 0.06	6.42 ± 0.06	1.000
$\Delta H^{\neq}$ (Kcal/mol)	12.5 ± 0.3	17.3 ± 0.5	
$\Delta S^{\neq}$ (cal/(mol K))	−20.2 ± 1.1	−14.4 ± 1.6	
r^a	0.999	1.000	

[a] Correlation coefficients.

the two kinetically significant processes must be acid-dependent, while there is a process independent of the thiourea concentration. From these results, k_{obs} can be written as

$$k_{obs} = (k_1|tu| + k_2)|HClO_4|^* \qquad (2)$$

By plotting the slopes of the straight lines $k_{obs}/|HClO_4|$, *i.e.* $(k_1|tu| + k_2)$, against $|tu|$, it is possible to separate the specific rate constants of the two processes. The values obtained at the four considered temperatures are reported in Table II, together with the thermodynamic parameters.

As one can see, the very good correlation coefficients show the reliability of the data treatment. It is also interesting to note that the activation enthalpy of the thiourea-dependent process is lower than that of the other.

Since the oxidant power of OsO_4 is well known [4], it is logical to think the solvent is involved in the non thiourea-dependent reduction process. To clarify this point of view, we have repeated the kinetic

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[*] Kinetic experiments carried out with the same conditions using as acid HBF_4 or H_2SO_4, buffered with the respectively sodium salts, have given different k_{obs}s, thus indicating a specific acid catalysis.

TABLE III. Pseudo-first Order Rate Constants ($k_{obs} \times 10^3$) for the Reduction of OsO_4 by Thiourea in Aqueous Perchloric Acid Solutions; $\mu = 0.981$.

$|HClO_4|$	$|tu| \times 10^2$	t °C			
		20	30	37	45
0.981	1.41	11.29 ± 0.08	22.84 ± 0.20	37.10 ± 0.42	62.12 ± 0.40
	1.06	9.00 ± 0.08	18.85 ± 0.32	31.31 ± 0.39	53.02 ± 1.00
	0.88	7.77 ± 0.08	17.07 ± 0.31	27.19 ± 0.43	46.55 ± 0.96
	0.53	5.39 ± 0.08	12.63 ± 0.20	19.82 ± 0.38	38.53 ± 0.62
0.785	1.41	9.23 ± 0.07	18.28 ± 0.22	29.95 ± 0.22	52.70 ± 0.41
	1.06	7.42 ± 0.06	15.67 ± 0.19	26.31 ± 0.18	46.12 ± 0.90
	0.88	6.75 ± 0.06	14.53 ± 0.17	23.14 ± 0.30	42.40 ± 0.52
	0.53	4.87 ± 0.08	10.83 ± 0.14	18.22 ± 0.43	35.42 ± 0.98
0.588	1.41	7.09 ± 0.04	15.25 ± 0.12	23.49 ± 0.11	40.95 ± 0.72
	1.06	5.95 ± 0.03	12.30 ± 0.10	20.03 ± 0.22	37.76 ± 0.48
	0.88	5.39 ± 0.03	11.54 ± 0.06	19.05 ± 0.19	34.90 ± 0.29
	0.53	4.21 ± 0.04	9.34 ± 0.12	15.81 ± 0.15	30.62 ± 0.52
0.392	1.41	4.86 ± 0.05	9.52 ± 0.08	16.83 ± 0.29	27.88 ± 0.23
	1.06	4.15 ± 0.03	8.53 ± 0.06	15.23 ± 0.25	26.00 ± 0.28
	0.88	3.86 ± 0.03	7.95 ± 0.05	13.99 ± 0.13	24.18 ± 0.22
	0.53	3.18 ± 0.01	6.88 ± 0.05	12.51 ± 0.23	22.23 ± 0.41

experiments in water, hoping to simplify the reaction mechanism, *i.e.* to make $k_2 = 0$.

Working in acid water with buffered ionic strength, it has been possible to evaluate the k_{obs}s as before. The k_{obs} s at various temperatures and at different concentrations of $HClO_4$ and tu are reported in Table III. Also here, the reaction is of the first order with respect to $[Os(tu)_6]^{3+}$. Contrary to what was expected, the kinetics were more complicated with respect to the H_2O/EtOH medium. In fact, as shown on the right side of the figure, the k_{obs}s are not linear with respect to the perchloric acid concentration, although the plots $k_{obs}/|HClO_4|$ clearly cross the origin. This means that the dependence of the k_{obs} on $|HClO_4|$ is not of the first order, and that all the kinetically significant processes must be acid-dependent. Hence k_{obs} can be written as

$$k_{obs} = k'_{obs}|HClO_4| \tag{3}$$

where, certainly, k'_{obs} still retains the acid concentration. In order to find the analytical expression of the k'_{obs}, the $k_{obs}/|HClO_4|$ values have been reported *versus* $|HClO_4|$ and $|tu|$, and in both cases the plots are straight lines with positive intercepts, *i.e.*:

$$k'_{obs} = a|HClO_4| + b \tag{4}$$

$$k'_{obs} = a'|tu| + b' \tag{5}$$

where a and b depend on the tu concentration and a′ and b′ on the acid concentration.

The analytical expression of a and b have been found by their plots *versus* |tu|; in the same way it is possible to know a′ and b′ by plotting them against $|HClO_4|$. In all cases, straight lines have been obtained, whose slopes and intercepts are the specific rates of the kinetically important processes. The specific rate constant values obtained from a and b or from a′ and b′ are the same.

By substituting the analytical expression of a′ and b′

$$a' = k'_1 + k''_1|HClO_4| \tag{6}$$

$$b' = k'_2 - k''_2|HClO_4| \tag{7}$$

in (5) or, in the same way, that of a and b

$$a = -k''_2 + k''_1|tu| \tag{8}$$

$$b = k'_2 + k'_1|tu| \tag{9}$$

in (4), and taking (3) into account, the complete dependence of k_{obs} on $|HClO_4|$ and |tu| is obtained:

$$k_{obs} = [(k'_1 + k''_1|HClO_4|)|tu| + (k'_2 - k''_2|HClO_4|)]\,|HClO_4| \tag{10}$$

From (10), it is possible to point out that there are four main processes, all acid-dependent; only two of them are thiourea-dependent. In Table IV, k'_1, k''_1, k'_2 and k''_2 are reported at the four considered temperatures, together with their activation parameters. As one can see, the two thiourea-dependent processes are faster than the other two and the step relative to k'_1 has a lower activation enthalpy than that of k''_1.

By comparison of eqns. (10) and (2), it is interesting to note that (2) can be derived from (10)

TABLE IV. Specific Rate Constants and Their Activation Parameters for the Reaction in Water.

t (°C)	$k'_1 \times 10$ (mol^{-2} l^2 sec^{-1})	k''_1 (mol^{-3} l^3 sec^{-1})	r[a]	$k'_2 \times 10^2$ (mol^{-1} l sec^{-1})	$k''_2 \times 10^2$ (mol^{-2} l^2 sec^{-1})	r[a]
20	3.53 ± 0.08	0.34 ± 0.01	0.999	0.79 ± 0.02	0.62 ± 0.02	0.999
30	4.82 ± 0.37	0.72 ± 0.05	0.995	1.82 ± 0.06	1.18 ± 0.08	0.996
37	7.40 ± 0.64	1.28 ± 0.09	0.995	3.46 ± 0.08	2.55 ± 0.12	0.998
45	9.37 ± 1.04	1.91 ± 0.14	0.994	6.44 ± 0.18	4.09 ± 0.25	0.996
$\Delta H^{\neq}$ (Kcal/mol)	6.9 ± 0.5	12.4 ± 0.5		15.0 ± 0.2	13.8 ± 0.8	
$\Delta S^{\neq}$ (cal/(mol K))	−37.0 ± 1.7	−18.3 ± 1.5		−16.9 ± 0.7	−21.7 ± 2.7	
r[a]	0.988	0.997		1.000	0.992	

[a]Correlation coefficients.

when k''_1 and k''_2 are equal to zero. Then, on passing from H_2O/EtOH to pure H_2O there is no substantial change in the reaction mechanisms, but in water two additional reactions are found, both depending on the second power of the $HClO_4$ concentration. The former, *i.e.* the thiourea-dependent one, is still a formation process of the complex, the latter regards its decomposition. Perhaps the different basicity of the two media might be responsible for the fact that the two mechanisms strongly depending on the acidity are present in water.

From eqn. (10) it should be possible to hypothesize the reaction mechanism which must account for the complicated dependence of the k_{obs} on $|HClO_4|$. If we consider the protonation equilibria both of thiourea [5] and of OsO_4, it is possible to write several reactions, some of which can be in agreement with the kinetic equations; for example, if the reaction occurs between the protonated thiourea (tuH^+) and OsO_4, then

$$v = k|tuH^+||OsO_4|. \qquad (11)$$

By substituting $|tuH^+|$ in terms of the protonation equilibrium constant of tu, (11) becomes

$$v = kK_{eq}|H^+||tu||OsO_4| \qquad (12)$$

where kK_{eq} is k'_1 of equation (10). k''_1 might be the specific rate constant of the reaction between both protonated tu and OsO_4.

To understand the process involving k'_2 in (10) or k_2 in (2) is much more difficult; at first, we have thought of a reduction of Os(VIII), followed by a fast coordinative process by means of EtOH; since this constant is still present in water, this point of view falls. Being dependent only on $|HClO_4|$ and on $|OsO_4|$, it is logical to think of a decomposition, of the S_{N1} type, of the protonated ion, OsO_4H^+, followed by fast steps of reduction to Os(III) and coordination of Os(III).

Experimental

Preparation of Acid Solutions

The osmium tetroxide solution was prepared only in water by weighing. The perchloric acid solutions were prepared in both media and tested by alkalimetric titrations. The thiourea and sodium perchlorate solutions were prepared by weighing.

The kinetic solutions were prepared, immediately before each experiment, by mixing the appropriate amounts of tu, $HClO_4$ and $NaClO_4$ in order to keep the ionic strength constant ($\mu = 0.981$).

Spectrophotometric Measurements

To a prethermostatted acid solution of tu, 100 μl of a OsO_4 solution was added directly in the measurement cell under stirring and the increase of the absorbance was recorded in time-drive, at the maximum wavelength of the complex (λ = 481 nm) until a constant value was reached. This final value of absorbance (A_∞) persists much longer in H_2O/EtOH than in H_2O solution, where the decomposition of the complex is faster.

Data Processing

The k_{obs} were obtained by slopes of plots of ln ($A_\infty - A_t$) against time.

In H_2O/EtOH, the k_{obs}s are straight lines *versus* $|HClO_4|$ crossing the origin. By plotting the slopes of these lines *versus* $|tu|$, k_1 and k_2 have been evaluated as slope and intercept respectively.

In H_2O, the k_{obs}s are straight lines *versus* $|tu|$. From these lines the slopes and the intercepts are calculated. These numerical values, divided by the acid concentration at all the concentrations, are reported against $|HClO_4|$. Once again, straight lines are obtained, whose slopes and intercepts are k'_1, k''_1, k'_2 and k''_2.

All the straight lines were calculated by the least squares method.

Acknowledgement

This work was supported by C.N.R. (Rome).

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