

THE KINETICS AND MECHANISM OF
OXIDATION OF THE N-SUBSTITU-
TED UREA-TITANIUM (III) COM-
PLEXES BY IODINE (AS I_3^-) IN
ETHANOL AND ACETONITRILE.

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(Received 30th May, 1987)

ABSTRACT

The oxidation of complexes of Ti(III), $(TiL_6)^{3+}$ (L=ur, Meur, DMeur, DEtur, N-Bu-ur, and Phur), by iodine as I_3^- in ethanol and acetonitrile solutions, appears to proceed as a second order reaction and is much faster in ethanol solution (where solvolysis occurs) than in acetonitrile. The enthalpy of activation appears to decrease as ligand's size increases which suggests that the kinetic stability of these compounds is not just because of steric hinderance; but electronic effect of the ligand must be more important.

The mechanism of the reaction is suggested to be an inner redox reaction in which an electron transfers through a bridge which is formed by bonding I_3^- to the complex ion.

INTRODUCTION

Titanium (III) is a sufficiently strong reducing ion which can be oxidized by many oxidising agents. The earliest reports discuss the kinetics of oxidation of Ti(III) by aqueous solutions of iodine (1,2). Their investigations were confined to fairly high concentrations of acid and iodide. A recent report shows a more complex acid dependence (3). This reinvestigated work studies the reaction over a wider range of reactant concentrations.

There are many other reports on oxidation of Ti(III) by oxidising agents (4-46). Among there, a review paper with 41 references discusses the use of Ti(III) as a reducing agent in analytical chemistry, the determination of Ti(III), the state of Ti(III) in aqueous solutions and methods for stabilization of Ti(III) by using neutral hetroaromatic ligands containing N (such as O-phenantroline) (5). Many Ti(III) oxidation reactions proceed via outer sphere mechanism (10,11). In some of them such as Ti(III)-Co(III) redox reactions electron-transfer occurs through a bridge which is made by the ligand (oxalate ion) (12). Earley, and ka -

llen (13) have suggested that "some of the remarkable properties of Ti(III) and Ru(II) (such as the ability to reduce perchlorate ion) can be understood as involving unusually extensive overlap between t_{2g} electron-donor and- acceptor orbitals. This effect should be more prominent in inner-sphere than in outer-sphere reactions. The magnitude of interaction between electron-donor and electron acceptor orbitals, in or prior to the transition state, should be important in deciding whether or not Marcus' theory is applicable and clearly would be important in the consideration of such reactions on a molecular orbital basis".

Among the Ti(III) redox reactions for which inner-sphere mechanisms have been demonstrated, those involving oxidants of less positive charge are more rapid than those involving oxidants of more positive charge (14).

EXPERIMENTAL PROCEDURE

Reactant solutions were prepared according to the following procedure: titanium N-substituted urea complexes were aliquots the solutions obtained upon their preparation (15); I_3^- solution was prepared by dissolving

iodine (A.R. grade) in ethanol or acetonitrile solutions containing potassium iodide, free from any impurities and gases, under nitrogen atmosphere. Rate measurements were made on an Aminco Morrow stopped flow spectrophotometer designing for faster reactions. More details of the technical treatments have previously reported (16). Solvents were purified by distillation, under nitrogen, from a suitable drying agent, i.e. ethanol, from magnesium ethoxide prepared in situ; acetonitrile, from molecular sieve, followed by P_2O_5 .

RESULTS AND DISCUSSIONS

All the oxidation reactions on Ti(III) have been carried out in aqueous solutions which makes the problem more complicated. But the present work is interesting because first, the reactions were occurred in an absolutely pure organic solvent, and second on a known complex that has already been prepared.

(a) Oxidation of $[Ti(ur)_6]I_3$ with KI_3 in Ethanol

The reaction was studied assuming pseudo-first-order conditions, with Ti(III) in excess (Figs 1, 2). Plots of k_{obs} versus $[Ti(III)]$ (Fig. 3) and $\ln k$

versus reciprocal temperature (Fig.4) were linear. The plot of k_{obs} versus $[Ti(III)]$ was in agreement with equation 1.

$$k_{obs} = k[Ti(III)] \quad 1$$

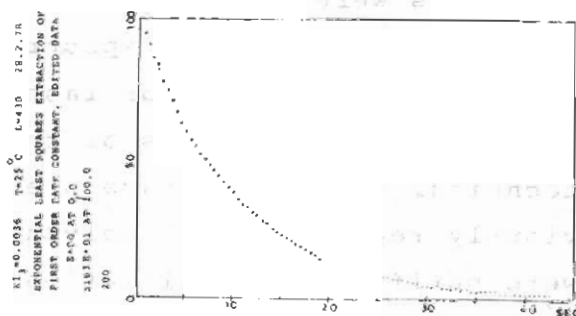


Fig.1. Variation of absorbance vs time for the oxidation of $[Ti(ur)_6]I_3^-$ by KI_3 at $25^\circ C$

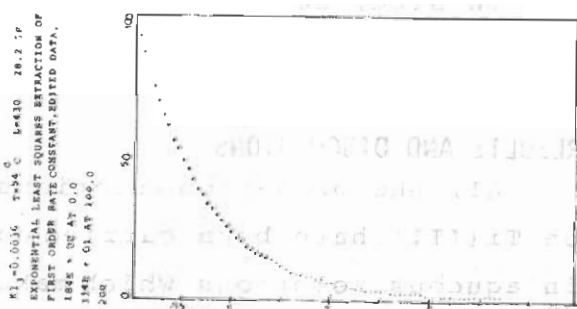


Fig.2. Variation of absorbance vs time for the oxidation of $[Ti(ur)_6]I_3^-$ by KI_3 at $54^\circ C$.

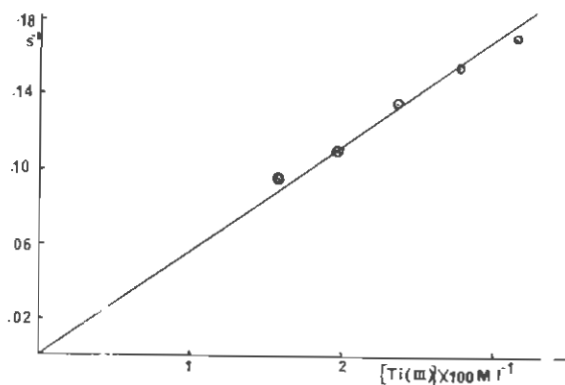


Fig.3. Variation of k_{obs} for oxidation of $[Ti(ur)_6]I_3^-$ by KI_3 vs $[Ti(III)]$

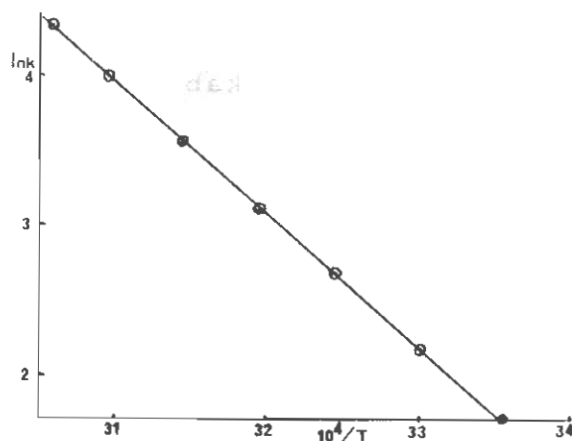


Fig.4. Arrhenius plot for oxidation of $[Ti(ur)_6]I_3^-$ by KI_3 .

Table 1. Variation of k vs temperature .

($[Ti(III)] = 0.036 M$ and $[I_3^-] = 0.0036 M$)

No. of Runs	Temp °C	$k_{obs} (ave)$ s^{-1}	k $l mol^{-1} s^{-1}$
2	25	0.100	5.56
2	30	0.159	8.53
2	35	0.260	14.44
2	40	0.400	22.22
2	45	0.629	34.94
2	50	1.000	55.65
2	55	1.400	77.87

The values of k (Table 1) were used to calculate the activation parameters.

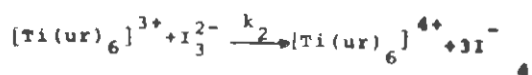
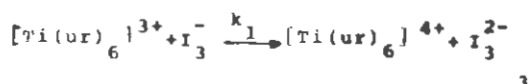
The oxidation reaction of $Ti(III)$ by iodine is one of the earliest reports of redox systems involving $Ti(III)$. This reaction and a similar one, oxidation by chlorine, and others were investigated in aqueous acid solutions (1-42).

In this work, the reaction of Ti(III) with I_3^- was carried out in ethanol. The reaction followed a second-order kinetics with a second-order rate constant $k=5.56 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C . The reaction is adequately described by equation 2. i.e. the reaction is first-order both in $[Ti(III)]$ and in $[I_3^-]$

$$- \frac{d[Ti(III)]}{dt} = \frac{-d[I_3^-]}{dt} = k [Ti(III)] [I_3^-] \quad 2$$

Since the solvent, ethanol, in comparison with urea is a weak donor, then the complex may exist mainly as

$[Ti(ur)_6]^{3+}$ ion in the ethanol solution. Therefore, equations 3 and 4 are suggested as the relevant oxidation steps for the reaction:



Although it is uncertain whether the Ti(IV) exists as $[Ti(ur)_6]^{4+}$ or in some other form. The suggested mechanism is in agreement with what has been suggested for the Ti(III)- Cl_2 and Ti(III)- I_2 systems (17,18).

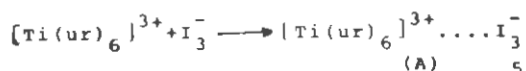
In general, halogen oxidation reactions are thought to proceed by the mechanism indicated by reactions 3 and 4.

Reversibility in the first step

(and the expected product inhibition) seems to depend on the free energy, ΔG° , for the first step. If the redox potential, E° for the $M^{n+}-M^{(n-1)+}$ couple is much less than for $X_2 - [X_2]^-$ ($X=I$ or Cl), ΔG° for the first step will be less than zero. The first step in such one electron changes will not be reversible in the kinetic sense, and inhibition by M^{n+} i.e. the oxidation product of the reaction, will not be observed.

However, if the converse is true, the first step will be reversible in the sense that M^{n+} will inhibit the reaction. The $V^{IV}-Cl_2$ and $V^{IV}-Br_2$ reactions $E^\circ(V^{IV}/V^{III})=1.00 \text{ V}$, $E^\circ(Cl_2/2Cl^-)=1.358 \text{ V}$, $E^\circ(Br_2/2Br^-)=1.065 \text{ V}$, which are strongly inhibited by V^V ; and $Fe^{II}-Br_2$ ($E^\circ(Fe^{3+}/Fe^{2+})=0.77 \text{ V}$), inhibited by Fe^{III} , produce good examples of the latter case (17-20). While Ti(III)- I_2 , $V^{III}-I_2$, $V^{III}-Br_2$, Ti(III)- Cl_2 are good examples of the former (21-24).

We now examine the mechanistic details of the reaction of $[Ti(ur)_6]^{3+}$ with I_3^- . The first step is probably the diffusion-controlled formation of a collision complex with the reactants trapped in the solvent matrix Eq(5).



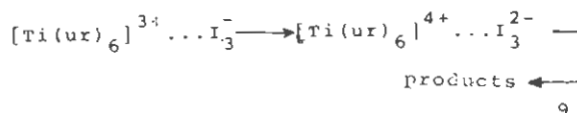
The entity (A) can then progress either through an inner-sphere path 6 and 7 giving precursor (B) and successor (C) complexes:



and the products:



or through an outer-sphere mechanism:



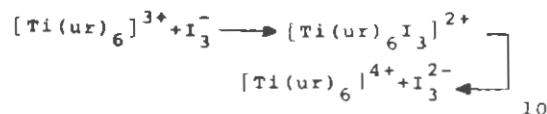
The binuclear specie will be termed an intermediate only if its life-time exceeds characteristic vibration times, and obviously in these situations the observed second-order rate constant and the associated activation parameters ΔH^\ddagger and ΔS^\ddagger will be composite values. The present oxidations also appear to correspond to the case where the first step is irreversible.

Since the redox rate constant is less than the substitution rate constant (Table 2) then electron transfer within the precursor complex will be rate determining

Table 2. Rate constants of some Ti(III) reactions at 25°C

Reaction		$k/\text{mol}^{-1}\text{s}^{-1}$	Reference
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$	(Sub)	10^5	40
$[\text{Ti}(\text{ur})_6]^{3+} + \text{H}_2\text{O}$	(Sub)	135	16
$[\text{Ti}(\text{ur})_6]^{3+} + \text{SCN}^-$	(Sub)	2770	16
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^-$	(Sub)	3980	41
$[\text{Ti}(\text{ur})_6]^{3+} + \text{I}_3^-$	(Ox)	5.55	this work
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} + \text{I}_3^-$	(Ox)	6.80	3

The mechanism of the reaction is suggested to be an inner redox reaction where in an electron transfers through the bridge bonding the I_3^- with the complexion



The following reactions were also studied, and their results are listed in tables 3, 4 and figs. 5, 6.

- (b) Reaction of $[\text{Ti}(\text{Meur})_6]\text{I}_3$ with KI_3 in acetonitrile.
- (c) Reaction of $[\text{Ti}(\text{DMeur})_6]\text{I}_3$ with KI_3 in acetonitrile.
- (d) Reaction of $[\text{Ti}(\text{DEtur})_6]\text{I}_3$ with KI_3 in acetonitrile.
- (e) Reaction of $[\text{Ti}(\text{nBu-ur})_6]\text{I}_3$ with KI_3 in acetonitrile.
- (f) Reaction of $[\text{Ti}(\text{Phur})_6]\text{I}_3$ with KI_3 in acetonitrile.
- (g) Reaction of $[\text{Ti}(\text{DEtur})_6]\text{I}_3$ with KI_3 in ethanol.

Table 3. Variation of k vs temperature for the oxidation of $[\text{Ti}(\text{DEtur})_6]\text{I}_3$ by KI_3 in ethanol.

$[\text{Ti}(\text{III})]=0.036 \text{ M}$ and $[\text{KI}_3]=0.0036\text{M}$ at $\lambda=430 \text{ nm}$.

No. of Runs	Temp °C	k_{obs} (ave) s^{-1}	k $\text{l mol}^{-1} \text{s}^{-1}$
4	25	0.800	44.48
3	30	1.241	48.96
3	35	1.713	95.15
2	40	2.372	131.70
2	45	3.853	214.04
4	50	5.705	316.96
4	55	7.967	442.62

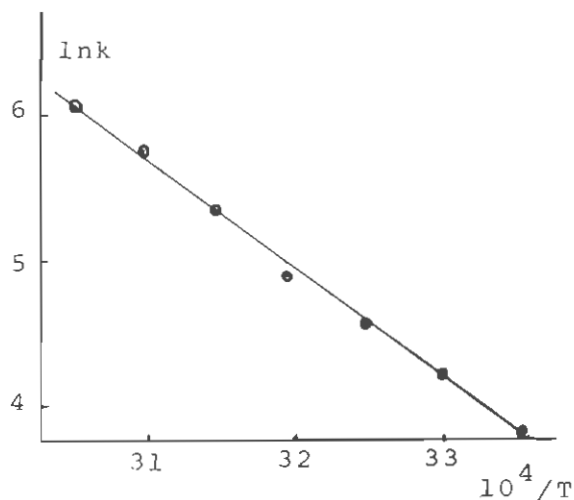


Fig.5. Arrhenius plot for oxidation of $[\text{Ti}(\text{DEtur})_6]\text{I}_3$ by KI_3

Table 4. The result obtained for the reactions.

Reaction	No. of Runs	Temp. °C	$10^3 k_{\text{obs}}$ (Ave) s^{-1}	$10^3 k$ $\text{l mol}^{-1} \text{s}^{-1}$
b-Reaction of $[\text{Ti}(\text{Meur})_6]\text{I}_3$ with KI_3 in acetonitrile	1	25	0.64	15.1
	1	30	1.43	33.6
	1	35	3.18	74.8
	2	40	6.79	159.9
	2	45	13.90	327.7
	2	50	29.20	687.7
c-Reaction of $[\text{Ti}(\text{DMeur})_6]\text{I}_3$ with KI_3 in acetonitrile	3	25	1.53	61.3
	1	31	2.32	93.0
	2	35	3.01	121.0
d-Reaction of $[\text{Ti}(\text{DEtur})_6]\text{I}_3$ with KI_3 in acetonitrile	2	35	8.2	171
	4	40	18.3	383
	4	45	33.8	709
	4	50	54.0	1130
	3	55	94.8	1983
e-Reaction of $[\text{Ti}(\text{n-Bu-ur})_6]\text{I}_3$ with KI_3 in acetonitrile.	2	35	2.84	47.57
	4	40	5.46	91.45
	4	45	9.26	155.23
	4	50	16.05	268.84
f-Reaction of $[\text{Ti}(\text{Ph-ur})_6]\text{I}_3$ with KI_3 in acetonitrile	2	35	1.34	44.70
	3	40	2.55	83.60
	1	45	3.96	129.18
	2	50	8.00	262.29
2	55	15.40	504.92	

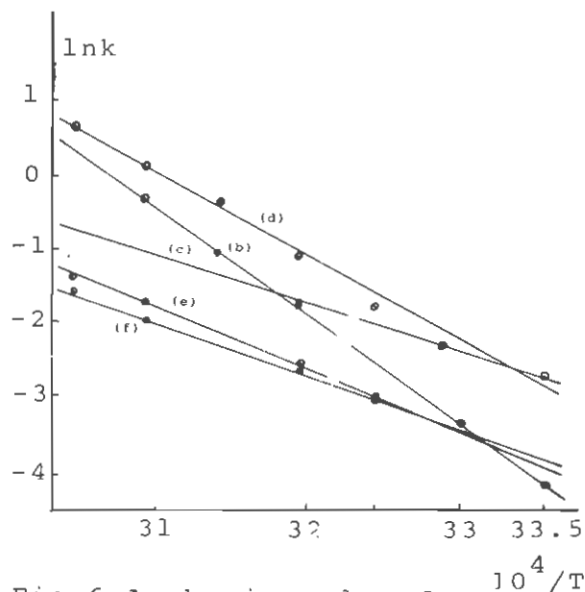


Fig.6. Arrhenius plot for oxidation of reactions b-f

Comparison the reactivities of the complexes

The second-order rate constants (at 25°C) and activation

parameters determined for the various reactions in the previous section are summarised in Table 5.

Table 5. Rate constants and activation parameters

Reaction	Solvent	k_{298} ($\text{l mol}^{-1} \text{s}^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)
$[\text{Ti}(\text{ur})_6]^{3+}$	EtOH	5.6	70.3	6.0
$[\text{Ti}(\text{Meur})_6]^{3+}$	MeCN	0.015	120	122
$[\text{Ti}(\text{DMeur})_6]^{3+}$	MeCN	0.061	47.6	-108
$[\text{Ti}(\text{DEtur})_6]^{3+}$	MeCN	0.067	97.7	59.0
$[\text{Ti}(\text{DBetur})_6]^{3+}$	EtOH	44.5	60.0	-12
$[\text{Ti}(\text{nBu-ur})_6]^{3+}$	MeCN	0.016	90.0	23
$[\text{Ti}(\text{Phur})_6]^{3+}$	MeCN	0.012	98.7	50

Considering now the oxidation reactions, the majority were carried out in acetonitrile since the solvolysis of the complexes in ethanol was too severe to allow oxidation studies. The two reactions in ethanol are seen to be generally much faster than the corresponding reactions in acetonitrile. In the case of the diethylurea complex, reactions in the two solvents are directly compared with the reaction in ethanol being some 70 times faster. The lower activation energy and negative ΔS^\ddagger in the ethanol solvent supports the occurrence of solvolysis prior to the oxidation step. It is quite plausible that the activating (rate determining) step in the ethanol-solvent oxidation is, in fact, a solvolytic step. This suggestion is supported by the generally rather unstable nature of these complexes in ethanol, evidenced by

the changes in visible region absorption spectra following dissolution of the complex.

The solutions in acetonitrile are much more stable; no changes in absorption spectra occur during the solution storage, which is in keeping with the expected relative solvolytic properties of EtOH and MeCN. Thus, it is likely that the mechanism involves a direct interaction between oxidant (I_3^-) and complex as already suggested (equations 5-10). However, not a straightforward relationship seems to exist among the reaction rate constants, activation parameters, and the nature (neither size nor inductive effect) of the alkyl substituent in the urea ligand. It seems clear that even a small change in reagent, such as the substitution of dimethylurea for methylurea, brings out a marked change in reaction type. However, direct comparison of the reactions of the methyl-, diethyl-, and n-butyl-urea complexes shows a steady reduction in both the ΔH^\ddagger and the (positive) ΔS^\ddagger along the series. Since increasing the size of the attached ligand would be expected, other things being equal, to increase the diffi-

culty of "approach" of I_3^- , to the complex, and hence increase the activation energy for this step, it must be concluded that factors other than steric ones (i.e. electronic factors) must be more important. However, these ligands become progressively weaker nucleophiles along the substituent group series: $H > Me > DEt > nBu$. Thus, substitution (and/or solvolysis) becomes more pronounced, but also, because the electron-donor capacity of the ligands decreases, the effective electron density at the Ti^{3+} center becomes smaller along the same series, perhaps with the result that the tendency to oxidation also reduces along the series.

However, it is also clear that the situation is not as simple as this discussion might suggest, as several features remain unexplained (particularly the apparently anomalous reaction of the dimethylurea complex). In order to determine the mechanism of all these reactions much more research would be needed before any further discussion becomes possible.

Definitions, Symbols, and Abbreviations

As far as possible, stan-

dard symbols and abbreviations (S.I. units and I.U.P.A.C. convention) have been used.

Abbreviations:

Me = CH_3 ; Et = C_2H_5 ; Pr = $n-C_3H_7$;
 Bu = $n-C_4H_9$; Ph = C_6H_5
 ur = urea, $CO(NH_2)_2$
 Meur = methylurea, $CO(NHMe)NH_2$
 Etur = ethylurea, $CO(NHEt)NH_2$
 DMeur = sym-dimethylurea, $CO(NHMe)_2$
 TetMeur = tetramethylurea, $CO(NMe_2)_2$
 Prur = propylurea, $CO(NHPr)NH_2$
 nBu-ur = n-butylurea, $CO(NHBu)NH_2$
 Phur = phenylurea, $CO(NHPh)NH_2$
 DEtur = sym-diethylurea, $CO(NHEt)_2$

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