# A KINETIC STUDY OF THE OXIDATION OF Ti(III) TO Ti(IV) IN HYDROFLUORIC ACID SOLUTIONS*

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## SUMMARY

The oxidation of Ti(III) to Ti(IV) has been studied in hydrofluoric acid at temperatures of 25°, 34.5°, and 41.5°C. The initial Ti(III) concentration was varied from 0.05 to 0.5 $M$ and the initial HF concentration from 0.25 to 2.0 $M$. In solutions with moderate HF/Ti(III) ratios, reaction rate orders of approximately unity were found for both Ti(III) and HF. There were also indications that the various Ti(III) fluoride complexes were oxidized at different rates. The low apparent activation energy (~6 kcal) was an indication of a rate determining step between ions of similar sign.

## INTRODUCTION

In a study of the self-dissolution rate of titanium metal in hydrofluoric acid, STRAUMANIS AND CHEN[1] reported the reaction to follow the equation

$$Ti + 3HF \rightarrow TiF_3 + \tfrac{3}{2}H_2 \tag{1}$$

Later, it was further noted that a very slow reaction was occurring in which Ti(III) was being slowly oxidized further to Ti(IV) by unionized hydrofluoric acid[2] according to the reaction,

$$TiF_3 + HF \rightarrow TiF_4 + \tfrac{1}{2}H_2 \tag{2}$$

A kinetic study of this latter reaction in hydrofluoric acid solutions is the subject of this investigation.

## EXPERIMENTAL

The titanium used in this study was obtained from Metal Hydrides, Inc. It was in the form of metal powder (65 mesh) with a nominal purity of 99.9%. All other chemicals were Fisher "Reagent" grade. Singly-distilled water was used to prepare solutions. The reactors were improvised from polyethylene wash bottles as shown in

Fig. 1. They were continuously purged at a constant rate throughout the studies with ultrapure (electrolytically-generated) hydrogen and maintained at constant temperature ($\pm 0.1^\circ$C) with a water bath. The initial Ti concentration (as Ti$^{3+}$) was varied from 0.05 to 0.5 $M$ and that of the hydrofluoric acid (after dissolution of the Ti according to eqn. (1)) from 0.25 to 2.0 $M$. The reaction solutions were prepared by placing a predetermined amount of Ti powder in the reactor with approximately 300 ml of H$_2$O,
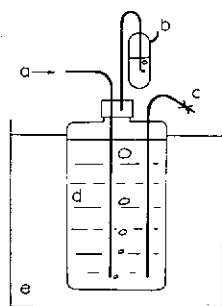


Fig. 1. Schematic diagram of reactors used in oxidation studies. (a, hydrogen inlet; b, water-sealed hydrogen outlet; c, sampling outlet; d, polyethylene reactor; e, constant-temperature water bath.)

then adding a predetermined amount of concentrated hydrofluoric acid in small portions, *ca.* 5 ml. (This latter precaution was necessary due to the vigor of the dissolution reaction.) When all the acid had been added, the reaction solution was diluted to 500 ml, the reactor placed in the water bath, and the hydrogen purge started. Periodically, a 10 ml portion of the solution was withdrawn and titrated with a standard KMnO$_4$ solution to determine the Ti(III) concentration. The experimental data could be reproduced within $\pm 5\%$. No dependence on the H$_2$ purging rate was noted.

RESULTS

Semilogarithmic plots of the Ti(III) concentration as a function of time for temperatures of 25$^\circ$, 34.5$^\circ$, and 41.5$^\circ$C are shown in Figs. 2–5. After an induction period, it can be seen that the plots in Figs. 2, 3(a), 4, and 5 are reasonably linear over extended periods of time. It can also be seen that there is a dependence on both Ti(III) and HF concentration. The continued linear decrease indicates that no equilibrium point is being approached during these periods. For these cases, the Ti(III) concentration is generally considerably less than that of the HF so that the semilogarithmic relationship suggests a first order dependence on the Ti(III) concentration with the effect of HF being shown in the change of the slopes of the lines. Thus, an empirical rate equation can be formulated as

$$-\frac{dC_{Ti^{3+}}}{dt} = kC_{Ti^{3+}}C_{HF}^{\alpha} \tag{3}$$

where: $C_{Ti^{3+}}$=Ti(III) concentration, g-mol/l; $C_{HF}$=hydrofluoric acid concentration, g-mol/l; $t$=time, h; $k$=rate constant, and $\alpha$=reaction order for hydrofluoric acid. $C_{HF}$ will be affected by several factors, among which are the amounts of HF used for

dissolution of the metal and for complexing both Ti(III) and Ti(IV) with F⁻. The quantity required for the metal dissolution can be readily calculated using eqn. (1) and was taken into account to give a desired HF concentration after the metal was dissolved. Work reported by CAGLIOTI, CLAVATTA AND LIBERTI[3] indicates that when
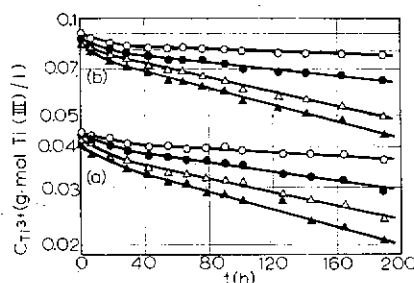


Fig. 2. Oxidation rate of Ti(III) to Ti(IV) in hydrofluoric acid at 25°C. (a) 0.05 $M$ Ti(III), (b) 0.10 $M$ Ti(III), (○, 0.25 $M$ HF; ●, 0.50 $M$ HF; △, 1.0 $M$ HF; ▲, 2.0 $M$ HF).
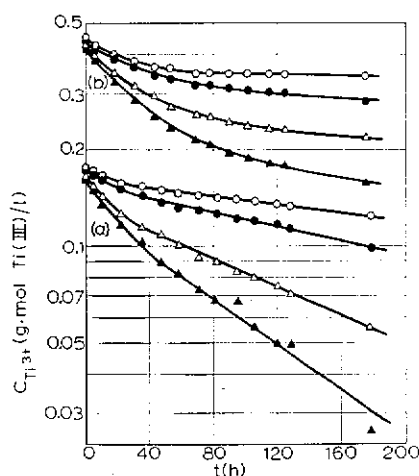
Fig. 3. Oxidation rate of Ti(III) to Ti(IV) in hydrofluoric acid at 25°C. (a) 0.20 $M$ Ti(III), (b) 0.50 $M$ Ti(III), (○, 0.25 $M$ HF; ●, 0.50 $M$ HF; △, 1.0 $M$ HF; ▲, 2.0 $M$ HF).
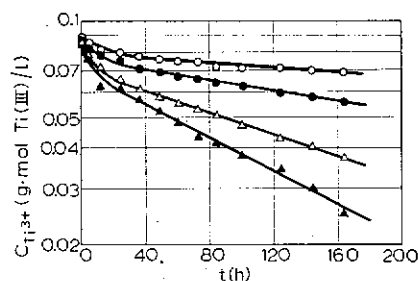


Fig. 4. Oxidation rate of 0.10 $M$ Ti(III) to Ti(IV) in hydrofluoric acid at 34.5°C. (○, 0.25 $M$ HF; ●, 0.50 $M$ HF; △, 1.0 $M$ HF; ▲, 2.0 $M$ HF.)
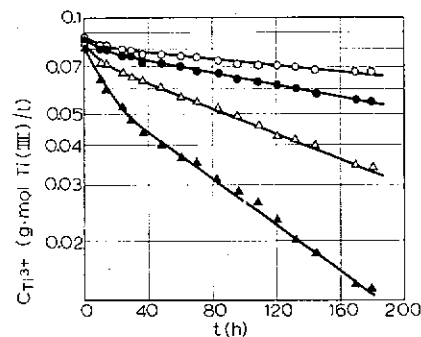
Fig. 5. Oxidation rate of 0.10 $M$ Ti(III) to Ti(IV) in hydrofluoric acid at 41.5°C. (○, 0.25 $M$ HF; ●, 0.50 $M$ HF; △, 1.0 $M$ HF; ▲, 2.0 $M$ HF.)

sufficient fluoride is present, Ti(IV) exists primarily as the $TiOF_4^{2-}$ species. Data pertaining to Ti(III) are very meager. Theoretical considerations indicate that up to six fluoride ions can be complexed and that in the presence of sufficient fluoride the most probable species is $TiF_6^{3-}$. With this information, the relation may be written

$$C_{HF} = C_{0_{HF}} - 4(C_{0_{Ti^{3+}}} - C_{Ti^{3+}}) - X \tag{4}$$

where, $C_{0_{HF}} =$ initial hydrofluoric acid concentration, $C_{0_{Ti^{3+}}} =$ initial Ti concentration,

and $X$ = concentration of hydrofluoric acid used to complex the Ti(III)*. Consideration of hydrofluoric acid equilibria and the $H^+$ production by the complexing reactions indicates that the concentration of unionized hydrofluoric acid (HF) is approximated by $C_{HF}$.

For some of the experimental conditions, $i.e.$, low Ti(III) and high HF concentrations, it can be seen that $C_{HF} \simeq C_{0_{HF}}$. This considerably simplifies the interpretation of the data as information pertaining to the fluoride complexes is not necessary and $C_{HF}$ can be assumed constant (and equal to $C_{0_{HF}}$). With this assumption, eqn. (3) can be written.

$$\frac{dC_{Ti^{3+}}}{C_{Ti^{3+}}} = -kC_{0_F}^\alpha \; dt \tag{5}$$

which can be integrated to give,

$$\log C_{Ti^{3+}} = -kC_{0_{HF}}^\alpha t + \text{constant} = -Bt + \text{constant} \tag{6}$$

This expression gives the relationship between $C_{Ti^{3+}}$ and $t$ suggested by the linear plots and it can also be seen, if the stated assumptions hold, that log–log plots of $B$ $vs.$ $C_{0_{HF}}$ should be linear and yield both the rate constant and the hydrofluoric acid reaction order, $i.e.$,

$$\log B = \alpha \log C_{0_{HF}} + k \tag{7}$$

Figures 6–8 are such plots. The effect of various degrees of complexing with $F^-$ is also shown in Figs. 6 and 7. From Fig. 6 (for 25°C), it appears that the HF concentra-
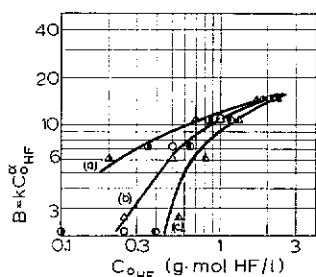


Fig. 6. Plot for the determination of the reaction order of hydrofluoric acid at 25°C. HF concentration calculated assuming Ti(III) is complexed with an average of (a) 6 $F^-$, (b) 3 $F^-$, and (c) o $F^-$. ( o, ◑, ◐, 0.05 $M$ Ti(III); △, ▲, ▲, 0.10 $M$ Ti(III).)
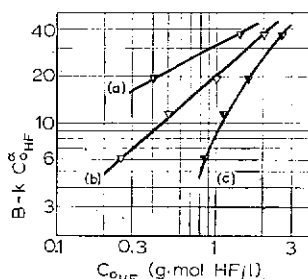
Fig. 7. Plot for the determination of the reaction order of hydrofluoric acid at 25°C for 0.20 $M$ Ti(III). HF concentration calculated assuming Ti(III) is complexed with an average of (a) 6 $F^-$, (b) 3 $F^-$, and (c) o $F$

tion order depends on the relative amounts of HF and Ti(III), $i.e.$, the HF/Ti(III) ratio. Though the slope, $\alpha$, is changing, it appears to be approaching a limit of approximately 0.5 for large HF/TI(III) ratios (> 10). In this region, complexing of the Ti ions would not significantly change $C_{HF}$.

For the region, $1 <$ HF/Ti(III) $< 10$ and at 25°C (Fig. 7), a linear plot with a slope of unity ($\alpha = 1$) is obtained using $C_{HF}$ equal to the initial HF concentration. This is equivalent to assuming that all Ti species are complexed with an average of three

* $0 \leq X \leq 6 \; C_{Ti^{3+}}$.

fluoride ions, thus leading to a relatively constant HF concentration. Figure 8 shows similar plots for $C_{0_{Ti^{3+}}} = 0.1$ (2.5 < HF/Ti(III) < 20) for all temperatures studied. The plots for the higher temperatures support a value of $x = 1$ and illustrate the decrease at 25°C at the high HF/Ti(III) ratios.

Numerous attempts were made to correlate the data shown in Fig. 3(b) (low HF/Ti(III) ratio), but all were unsuccessful. The specific rates in these solutions were somewhat less than in solutions containing lower Ti(III) concentrations.
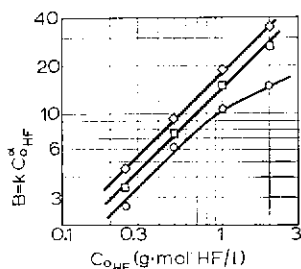


Fig. 8. Plot for the determination of the reaction order of hydrofluoric acid for 0.10 $M$ Ti(III) assuming Ti(III) is complexed with an average of 3 F⁻. ( ○, 25°C, □, 34.5°C, ◇, 41.5°C.)

DISCUSSION

The results of these studies generally support an oxidation rate of Ti(III) to Ti(IV) in hydrofluoric acid that is first order in respect of both Ti(III) and HF concentrations. Deviations from this behavior were found in three areas,

(1) during the initial portion of the reaction (an induction period),
(2) at high HF/Ti(III) ratios (>10) at the lower temperature, and
(3) at low HF/Ti(III) ratios (<2).

Needless to say, this leaves a somewhat limited range of applicability for the rate expression, but its consideration may be partially justified due to the very large number of correlations that were tried without any success. A large number of the attempts were made with computing facilities in which wide ranges of assumed equilibrium data for the complexes could be utilized*. With this in mind, the first order relationships will be accepted for the normal (uncomplicated) oxidation rate and an attempt will be made to explain the deviations.

First, are the long (10–30 h) induction periods. Here the rates are faster than predicted by the first order relationships. A partial explanation was first sought in the initial temperature of the reaction solutions and/or the presence of dissolved oxygen. With regard to the former, due to the considerable heat evolved during the metal dissolution, the initial temperature rose to 50°–60°C despite precooling of the solutions before mixing. However, direct measurements indicated that it approached that of the water bath in approximately 1 h. With regard to dissolved oxygen, the purging rate of hydrogen was such that any air remaining after the initial evolution of hydrogen by the metal dissolution would have been removed in a few minutes. Thus, neither of these could account for but a small portion of the induction period. What seems more probable (and will also account for the other deviations) is that Ti(III) complexes are

* Actual equilibrium data are not available from the literature. However, data available for Zr and Ti(IV) give relative magnitudes from which to initiate assumed values.

being formed at rates that are not a great deal faster than that at which they are being oxidized, and that the different complexes are oxidized at different rates. This would support a more stable, highly-complexed, species (lesser tendency to be oxidized at high HF/Ti(III) ratios) with their oxidation possibly associated with a partial dissociation of the complex ($x < 1$).

Similarly, the lower specific rates of the solutions in Fig. 3(a) (low HF/Ti(III) ratios) could be associated with a competition for HF between oxidation and complex formation of the Ti(III). For this case, the HF concentration becomes very low after the Ti(III) is complexed to a relatively small extent, thus effectively stopping further oxidation.

The Arrhenius activation energy (apparent) was calculated using rate constants taken from Fig. 8. The value was quite low, approximately 6 kcal. This, however, is consistent with what MOELWYN-HUGHES describes as "slow reactions", *i.e.*, those in which the reaction rate is small compared with the calculated collision frequency of species with sufficient energy to react[4]. There are several possible causes for the slowness of these reactions. Those which may be applicable here are:

(1) endothermic formation of a complex prior to the reaction proper,
(2) ionization of either of the reactants,
(3) stringent conditions of orientation, and
(4) strong forces of repulsion.

Any of these could be affecting the Ti(III) oxidation. Though it is not possible to make definite distinctions in this case, most reported examples of such slow reactions are between ions of like sign.

## ACKNOWLEDGEMENT

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