Kinetics of the Catalytic Oxidation of $p$-Phenetidine with Chlorate and the Role of the Catalyst Vanadium(V)

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With 7 Figures

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The oxidation of $p$-phenetidine hydrochloride (PHEN) with chlorate in the presence of vanadium(V) as catalyst has already been used as a model reaction in a number of studies of analytical catalytic methods\textsuperscript{1-6}. The aim of the present work is to discuss the kinetics of this reaction and the role of the catalyst in it.

Experimental

The product of the model reaction is intensely coloured\textsuperscript{2} and we used a photometric method to follow the kinetics of the reaction. The reagents, placed in a glass vessel with three sections\textsuperscript{7} (Fig. 1), were heated in a thermostat for 15 minutes and then mixed by vigorous shaking. The solution was placed in the cell of the photometer (FEK-M), which was equipped with a device for constant temperature regulation\textsuperscript{8}.

The optical density of the solution was followed as a function of the time for a period of some 10–15 minutes. During this period less than 1\% of the initial PHEN is used up and thus the kinetic equation

$$
\frac{dx}{dt} = k (C_0 - x)
$$

could be simplified to

$$
\frac{dx}{dt} = k \cdot C_0,
$$

where $C_0$ is the original concentration of PHEN, and $x$ is the amount of it oxidised in time $t$. 
In the optical density range used, the Bouguer-Lambert-Beer law is valid and equation (2) becomes

\[ \frac{dE}{dt} = k \cdot \varepsilon \cdot l \cdot C_0, \tag{3} \]

where \( E \) is the optical density, \( \varepsilon \) the molar extinction coefficient and \( l \) the cell width.

In the initial reaction period where \( x \ll C_0 \) the optical density would be increase linearly with time. The reaction rate constant could be determined from the slope of the graph of \( E \) against \( t \).

The solutions were prepared from reagent grade ammonium meta-vanadate and potassium chlorate. The \( p \)-phenetidine (A. R.) was twice distilled in vacuo and its hydrochloric salt made by adding specially purified hydrochloric acid. The \( p \)-phenetidine hydrochloride so formed was washed with ether and alcohol.

A buffer (pH 3.7) was made from reagent grade potassium hydrogen phthalate and specially purified hydrochloric acid.

All solutions were prepared with redistilled water.

The absorption spectra were taken on an SF-10 recording spectrophotometer.

**Results and Discussion**

**Mechanism of the catalyst action. Kinetic data**

The mechanism of the catalytic action could be clarified after the elucidation of the role of each of the reagents.

Vanadium(V) even in very low concentrations oxidizes PHEN in a slightly acid medium to coloured products, being reduced itself to vanadium(IV). In the absence of a catalyst, potassium chlorate does not react with PHEN and it was supposed that it reoxidizes the vanadium(IV) to vanadium(V), thus completing the reaction cycle.

Spectrophotometric studies showed that the oxidation of vanadium(IV) with chlorate proceeds very easily in slightly acid medium. A \( 10^{-2} \text{ M} \) solution of potassium chlorate oxidizes vanadium(IV) at 80\(^\circ\)C and pH 3–4 even when the concentrations are very low (\( 10^{-5} \text{ M} \)). The reaction is complete in less than 2 minutes and no detectable amounts of V(IV) could be found in the system after that. Under the same conditions vanadium(V) (\( 2 \cdot 10^{-4} \text{ M} \)) takes more than an hour to react with PHEN (\( 2 \cdot 10^{-3} \text{ M} \)).

In some experiments\(^9\) on the catalytic oxidation of PHEN vanadium(V) was replaced by the same amount of vanadium(IV). In these cases no difference in the reaction rate was found. This fact confirms that the oxidation of V(IV) to V(V) by potassium chlorate is very fast and is not the rate-determining step.