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The Chemistry of Uranium. Part XXIV. The Oxidation of Uranium(IV) Thiocyanate in Ethanol

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Introduction

Previous studies dealing with the oxidation of uranium(IV) by molecular oxygen have nearly exclusively been made in aqueous media. Thus Halpern and Smith [1] studied this reaction in an aqueous perchloric acid medium and proposed a free radical mechanism for it, the type of which was first postulated by Haber and Weiss in 1934 [2]. This mechanism, however, was not supported by the results of tracer experiments of Gordon and Taube [3]. Also a significant difference in the reaction rate in sulphate and perchlorate media made this mechanism somewhat dubious [4]. A survey of reactions with molecular oxygen was given by Fallab [5]. The question of possible intermediates in the reaction appeared to be of particular interest in view of the fact that the overall reduction of oxygen requires four electrons, while the overall oxidation of uranium(IV) involves a net loss of two electrons. In contrast to the observation in aqueous media, the reaction was found to be of second order with respect to uranium in toluene [6].

In the course of our studies on uranium(IV) compounds a marked decrease in stability of UX_4 compounds (X = Cl, Br, NCS) in alcoholic solution towards oxidation was observed compared with solutions in acetone. The present work was planned to contribute to the elucidation of the mechanism of the oxidation by obtaining data for the reaction rate of $U(NCS)_4$ with O_2 in ethyl alcohol.

Experimental

UCl_4 was prepared by reductive chlorination of UO_3 with hexachloropropene [7]. Absolute ethanol (Merck) was deoxydized by distilling it under nitrogen. Solutions of UCl_4 in ethanol were treated with stoichiometric amounts of a concentrated ethanolic solution of KNCS (Merck P.A.), the precipitate of KCl was removed by filtration, giving a clear solution of $U(NCS)_4$. Oxygen was supplied by Afrox and dried in a column filled with silica gel before use.

The experiments were carried out in a reaction vessel, thermostatted at 25 °C. Ethanol was saturated with oxygen by bubbling it through the solvent through a sintered glass plate. The flow rate was maintained at such values that alterations of it did not affect the observed rate of reaction. After saturation the solution of $U(NCS)_4$ was added quickly giving concentrations of uranium(IV) between 2×10^{-2} and 3×10^{-3} mol dm^{-3}. A Beckman DK2A spectrophotometer fitted with a flow cell (1 cm) was used to measure the decrease in absorbance at 1010 nm due to the uranium(IV).

Results and Discussion

Stoichiometry

The molar conductance curve of $U(NCS)_4$ in ethanol is typical for a weak electrolyte. Its electronic spectrum in solution (broad bands of relatively high extinction coefficients) suggest that the predominant species are moieties of high coordination number ($\geqslant 8$). Spectrophotometric measurements indicated that uranium(IV) and (VI) were the only significant uranium species present in the solution at any time during the reaction. The nature of the species in solution is not yet established.

Kinetics

A typical plot of absorbance *versus* time is shown in Figure 1. The partial oxygen pressure and hence its concentration in solution remained constant during the experiments. The change in reaction rate thus reflects the changing concentration of uranium (IV). The linearity of the curves obtained by plotting ln(absorbance) *versus* time (Figure 2) indicates the reaction to be of first order with respect to uranium (IV).

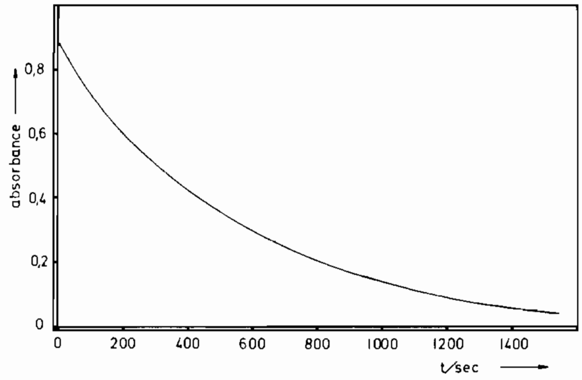

Figure 1. Absorbance *vs.* time plot for the oxidation of $U(NCS)_4$ with molecular oxygen.

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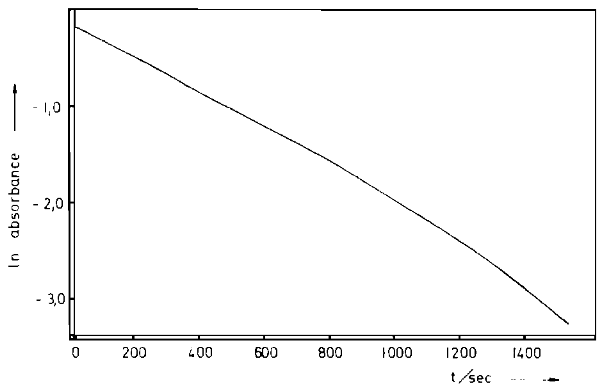

Figure 2. Pseudo first-order rate plot for the oxidation of $U(NCS)_4$ by molecular oxygen.

It was found, however, that the pseudo-first-order rate constant k_{obs} was not independent of the initial concentration of uranium(IV). It seems that k_{obs} is proportional to $1/\sqrt{[U]_0}$ in the concentration range under investigation with $k_{obs} = 2.255 \times 10^{-4}$ sec^{-1} $mol^{-1/2}$ $dm^{3/2}$. This is similar to the observation that k_{obs} for the oxidation of $U(SO_4)_2$ in aqueous sulphuric acid depends on the initial uranium concentration [4], while in a perchloric acid medium no such dependence was found [1]. As can be seen from Figure 2, first order kinetics are not applicable in the final stages of the reaction. These observations seem to signify that the reaction is not a simple first order process with regard to uranium(IV).

Reactions in a closed system, effected by mixing solutions of $U(NCS)_4$ and O_2 in as near as possible the stoichiometric amounts and subsequent treatment of the data by the method of Powell [8], proposed the reaction to be of an overall order of 3/2. Carrying out the reaction in solutions containing known amounts of water (up to 5%) resulted in an increase of the observed first-order rate constant, but no simple relationship could be established between k_{obs} and the concentration of water. This might be due, at least partly, to the fact that the solubility of O_2 in ethanol shows a marked dependence on the concentration of H_2O in the alcohol, but the data supplied by the literature [9] is insufficient to compensate efficiently for that. In toluene, however, where the reaction is of second order in uranium, water is reported to decrease the reaction rate [6]. Hydrolysed species of uranium(IV) are generally accepted to be the reactive species in aqueous solution. But if we assume this to be the case in alcoholic solution too, we should expect a decrease in reaction rate due to protons which are probably released during the reaction according to the equation:

$$2U(NCS)_4 + O_2 + 2H_2O \rightarrow 2UO_2(NCS)_2 + 4H^+ + 4NCS^-$$

Even if we pay regard to the observation of Murray-Rust *et al.*, who in 1929 found that the acidity of HNCS in C_2H_5OH is appreciably lower than it is in H_2O [10], thus acting as a buffer system, the pH of the solution should decrease considerably during the reaction resulting in a decrease in the concentrattion of hydrolysed uranium species shown by a slowing down of the reaction rate. This is, however, not observed, which cannot readily be explained. Thus far, the exact nature of the reaction product could not yet be established. It cannot, therefore, be excluded that solvolyzed species of uranium(IV) are involved in the rate determining step, since when a concentration term in the rate law appears to the power of plus or minus one half, the moiety included or discarded from the transition state may be derived from the solvent rather than from the species that appears in the rate law [11], which seems to assist the assumption that some kind of equilibrium exists where the solvent is involved.

This kinetic study of the oxidation of uranium(IV) in non-aqueous solution indicates that the small amount of water, which is always present, plays a major role. This fact complicates such studies considerably.

Acknowledgments

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