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Photo-oxidation of Isopropanol by Uranyl Perchlorate in Aqueous Acid Medium

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Photochemical oxidation of isopropanol by uranyl perchlorate in aqueous perchloric acid (1·0 *M*) was studied with visible light of wavelength 436 mμ at 35°C. The reaction was followed by measuring the rate of uranous ion production which was found to be proportional to light intensity and to light absorption fraction by the active species. Hydrogen ion concentration, ionic strength, initially added product (acetone) and temperature were found to have no effect on the rate. Initially added U^{4+} decreased the rate slightly acting as an internal filter. Formation of an intermediate complex between uranyl ion and isopropanol is suggested. Excitation of the complex by light, in a primary photochemical act, and decomposition of the excited complex by electron transfer mechanism in the dark are suggested to explain the mechanism of oxidation.

THE photochemistry of uranyl ions was and still is a subject of considerable research. Uranyl ions were employed to sensitize the photo-oxidation of many organic and inorganic compounds. The photochemical decomposition of uranyl oxalate in oxalic acid (actinometry) was studied in great detail[1]. Notwithstanding a lot of work in this field, the mechanism of the photosensitizing action of uranyl ions has remained obscure. A mechanism based on formation of excited uranyl ion (primary photochemical act) and energy transfer from the former to the substrate was postulated by West *et al.*[2] on the basis of fluorescence quenching studies. Further investigations, chiefly by Leighton and Forbes[3], however, proved that there was complex formation between uranyl ion and substrate. The complex absorbed light and formed an excited complex in a primary photochemical act, and decomposition of the latter in the dark yielded the products. The formation of U^{4+} during the course of the reaction indicated the possibility of electron transfer from the substrate to the uranyl ion. Experimental confirmation of such a mechanism was adduced by Heidt and Moon[4] in their studies on oxidation, by uranyl ions, of sucrose and other sugars and of methanol by Heidt[5]. An overall picture of the mechanism of photochemistry of uranyl ions appears to comprise one or more of the three processes: (i) energy transfer from the excited uranyl ion to the substrate; (ii) electron transfer from the substrate to the excited uranyl ion; and (iii) photo-oxidation of the substrate by oxygen in the system sensitized by uranyl ions. Process (iii) takes place in undeaerated systems where dissolved oxygen acts as the oxidizing agent. Uranyl ion oxidizes the substrate getting itself reduced to U^{5+} which immediately gets oxidized again to the U^{6+} state by the dissolved oxygen in the system. We have studied the photo-oxidation of isopropanol by uranyl ions in aqueous acid media in visible light of wavelength 436 mμ at 35°C. The reaction was followed by measuring rate of uranous ion production under conditions of variations of light intensity, light absorption fraction by the active species (by variation of [uranyl ion]), [alcohol], $[H^+]$, ionic strength, etc. The experimental results were compared with those obtainable from a prima facie reaction scheme involving excitation of either uranyl-substrate complex or uranyl ion alone, as a primary photochemical act, followed by electron transfer from the substrate to the uranyl ion, either in the former or in the latter, in the dark, leading to reaction products. It has been concluded that the excitation of uranyl substrate complex and subsequent electron transfer reaction is adequate to explain the mechanism of uranyl sensitized oxidation of substrates.

Experimental Procedure

Materials — Isopropanol (AR, BDH) was once distilled and used. Uranyl nitrate (AnalaR, BDH), perchloric acid (GR, E. Merck, 60 per cent) and distilled water [distilled twice over alkaline permanganate in an all glass set up and passed through 'Deminrolit' resin (Permutit, UK)] were used for the preparation of reagents.

Preparations and estimations — Uranyl perchlorate was prepared[4] by fuming uranyl nitrate repeatedly with concentrated perchloric acid, till all the volatile acid was removed and diluted to a stock solution (1·0*M*). Uranyl content of the solution was estimated by Jone's reductor method[6] and the free acid by ion-exchange method[7]. Uranous perchlorate, prepared by electrolytic reduction of the uranyl salt solution, was estimated titrimetrically with standard permanganate. Sodium perchlorate stock solution (5*M*) was prepared by neutralizing perchloric acid by sodium hydroxide with a *p*H meter.

Optical arrangements — The light source used was 250 W. high pressure mercury vapour lamp (Mazda ME/D; BTH, UK, box type fitted with glass window) which was connected to the mains through a choke and a voltage stabilizer. The optical arrangements were similar to those employed by Sheriff and Santappa[8]. The reaction cell, which was a rectangular glass vessel with optically flat and clear pyrex plates (1·0×2·5 cm.) cemented at both ends (optical path 3·8 cm.) and fitted with an outlet tube (B-10 socket), could be placed in the cell holder of the

Hilger-Watts spectrophotometer (H-700 type) directly for taking absorbancy measurements. The light absorption fractions of the reaction solution were calculated from the absorbancy values; variations in the former being accomplished by variations in the concentration of uranyl ion. The intensity of light was measured by uranyl oxalate actinometry. The reaction was followed by measuring the concentration of uranous ion formed from the values of absorbancy of the system at 670 mμ, the absorption peak for the uranous ions and after reference to a calibration curve. In a typical experiment, the reaction mixture containing uranyl perchlorate (5×10^{-3} to $3{\cdot}5\times10^{-2}M$), perchloric acid ($1M$), isopropanol (5×10^{-3} to $5\times10^{-4}M$) and sodium perchlorate ($\mu = 1{\cdot}25M$), was taken in the reaction cell and deaerated by passing oxygen-free nitrogen through the solution for about 20 min. The cell was then stoppered and irradiated with light of wavelength 436 mμ for fixed intervals of time, usually 3-10 min. The rate of formation of U^{4+} was followed with respect to time.

Results and Discussion

In all the experiments, the reaction was followed only up to 5 per cent reduction of U^{6+} to U^{4+} so that initial rates could be computed from slopes of $[U^{4+}]$ versus time plots. The plots were linear with a tendency for curvature only at high conversions (Fig. 1). The initial rates of the reaction, $d[U^{4+}]/dt$, were found to be proportional to light absorption fraction raised to 1·2 powers or $k_\epsilon^{1{\cdot}2}$ and to light intensity (Fig. 2). The quantum yield for the U^{4+} production increased slightly with increase in k_ϵ and remained constant for variations in light intensity, I. In the presence of oxygen, i.e. under undeaerated conditions, there was no U^{4+} production even after long exposures. There was no thermal dark reaction and the reaction showed no induction period under deaerated conditions. The rate of the reaction, as well as the quantum yield for U^{4+} production increased with [isopropanol] but a maximum rate was attained when [alcohol] $\geqslant 1{\cdot}0M$ with $[U^{6+}] = 0{\cdot}025M$ (Fig. 2). The plot of log $d[U^{4+}]/dt$ versus log [isopropanol] was not linear, indicating complexity of order with respect to [isopropanol] (Fig. 2). On the other hand, the plot of $(d[U^{4+}]/dt)^{-1}$ versus [isopropanol]$^{-1}$ was linear with an intercept on the Y-axis, indicating the presence of complex formation. Variation of $[H^+]$ ($pH < 2{\cdot}0$ to avoid hydrolysis of uranyl ions) was found to have no effect on the reaction rate. Ionic strength and temperature had little effect on the reaction rate. Initially added U^{4+} (product) acted as an internal filter and reduced the rate, while the initially added acetone (also product) did not affect the rate at concentrations of the latter equal to that of isopropanol. At high concentrations, initially added acetone slightly increased the rate, showing that the oxidation of acetone may occur by uranyl ions.

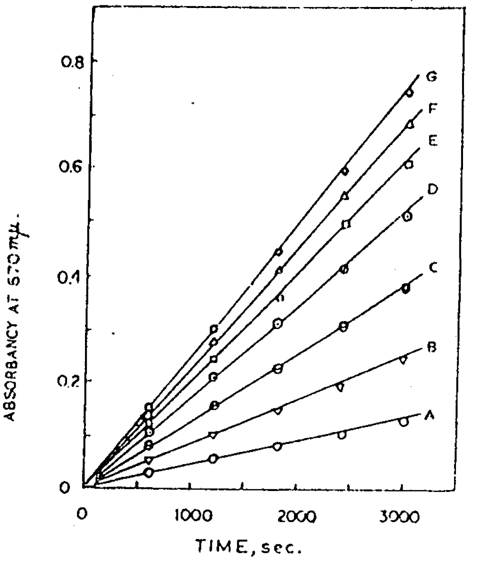

Fig. 1 — Absorbancy of U^{4+} at 670 mμ versus time plots at various uranyl ion concentrations

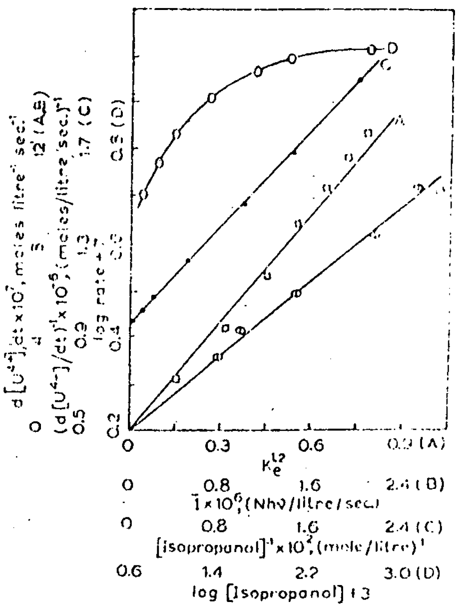

Fig. 2 — Curves showing the relation between initial rate of the reactions $d[U^{4+}]/dt$ and (A) light absorption fraction (k_ϵ); (B) light intensity (I) (C) [isopropanol]$^{-1}$; and (D) log [isopropanol]

The following reaction scheme represents the reaction steps most likely to occur:

$$\text{(i)}\quad UO_2^{2+} + S \overset{K_1}{\rightleftharpoons} UO_2^{2+}S$$

where S is the alcohol molecule and $UO_2^{2+}S$ is the photosensitive cluster.

$$\text{(ii)}\quad \text{(a)}\quad UO_2^{2+}S + h\nu \underset{k_d}{\overset{k_\epsilon' I}{\rightleftharpoons}} UO_2^{2+}S^*$$

$$\text{(b)}\quad UO_2^{2+} + h\nu \underset{k_f}{\overset{k_\epsilon'' I}{\rightleftharpoons}} UO_2^{2+*}$$

where k_ϵ' and k_ϵ'' are the light absorption fractions of photosensitive cluster and uncomplexed uranyl ions, 'I' the total light intensity, and k_d and k_f are the rate constants for the back reactions.

(iii) $UO_2^{2+}S^* \xrightarrow{k_1} UO_2^+ + \dot{S} + H^+$

(iv) $2\dot{S} \xrightarrow{k_2} S + \text{product}$

(v) $2UO_2^+ + H^+ \xrightarrow{k_5} UO_2^{2+} + UO(OH)^+$

(vi) $UO(OH)^+ \xrightarrow{\text{fast}} \text{stable } U^{4+} \text{ species}$

(vii) $UO_2^+ + \dot{S} \xrightarrow{k_7} UO(OH)^+ + \text{product}$

Assuming steady state conditions and $d[UO_2^{2+*}]/dt = 0$, $d[\dot{S}]/dt = 0$, $d[UO_2^+]/dt = 0$, $d[UO_2^{2+}S^*]/dt = 0$, etc., and assuming that the formation of $UO_2^{2+}S^*$ and UO_2^{2+*} are the primary photochemical acts, it follows

$$d[U^{4+}]/dt = k_1 k_c' I/(k_1 + k_d) \qquad \ldots(1)$$

The light absorption fraction by the cluster, expressed in terms of total light absorption fraction, $k_c(= k_c' + k_c'')$, and assuming that the extinction coefficients of the cluster and free uranyl ion are the same, is given by

$$k_c' = k_c(K_1[S]/1 + K_1[S]) \qquad \ldots(2)$$

so that Eq. (1) becomes,

$$d[U^{4+}]/dt = \frac{k_1 k_c I}{(k_1 + k_d)} \cdot \frac{K_1[S]}{1 + K_1[S]} \qquad \ldots(3)$$

This explains the first order dependence of rate on k_c and I. And Eq. (4)

$$(d[U^{4+}]/dt)^{-1} = (k_1 + k_d/k_1 k_c I)(1 + 1/K_1[S]) \ldots(4)$$

implies that reciprocal rates plotted against reciprocal [isopropanol] should be a straight line, and this was substantiated by experimental results. Step (ii) (B) has not been considered since it does not involve in any U^{4+} producing step and further, if UO_2^{2+*} ions reacted with the substrate directly, then the order with respect to $[UO_2^{2+}]$ should be 1, which was not the case. $K_1 = 185 \cdot 5$ lm^{-1} is calculated from intercept/slope of plot 1/rate versus 1/[S] (Fig. 2) and quantum yield for U^{4+} production, $\phi_{max} = 0 \cdot 596$, has been obtained. The ϕ_{max} value compares well with those for the oxidation of sugars and methanol ($\phi_{max.} \sim 0 \cdot 6$ for sugars[4] and 0·5 for methanol[5] both at 2537 A.). In both the above oxidations, the reaction was assumed to pass through the intermediate formation of a photosensitive cluster, which absorbs light (primary photochemical act) and decomposed to give U^{5+} ion (dark reaction). The formation of U^{5+} ion was proved beyond doubt and it was shown that U^{5+} disproportionated to U^{4+} and U^{6+} by a fast dark reaction. The plots of log $d[U^{4+}]/dt$ versus log k_c gave a slope of 1·2, instead of 1, as required by the rate expression. This discrepancy is explained as follows. The variation of k_c was effected by variation of uranyl ion concentration, which incidentally increased the photosensitive cluster also and accounted for the increase in the order with reference to k_c. It would no doubt be more appropriate to vary k_c by varying the light path of the reaction cell. But difficulties were encountered in the fabrication of such a cell, especially for following the rates in a spectrophotometer. The independence of the rate or reaction with respect to $[H^+]$ variation clearly indicated that there was no equilibrium involving H^+ and either uranyl ion or isopropanol in the pH range 0-2·0. The absence of any temperature dependence on reaction rate clearly indicated that the reaction was probably a pure photochemical one.

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