

Photooxidation of cellulose acetate and cellobiose by the uranyl ion

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The photooxidation of cellulose acetate by uranyl nitrate in acetone solutions has been investigated. Studies of the effect of the polymer on the uranyl luminescence showed an initial increase in intensity, followed by quenching. This is interpreted in terms of competition between complexation of uranyl ions by the polymer and dynamic quenching. In the quenching region, Stern–Volmer kinetics are followed. Upon photolysis of the solution, a decrease in viscosity was observed, consistent with chain scission. However, there was no sign of formation of reduced uranium species, suggesting that they are reoxidised by molecular oxygen. Model studies were carried out with cellobiose and it was confirmed that the luminescence quenching involves both dynamic and static processes. Photolysis of aqueous solutions of cellobiose and uranyl nitrate or perchlorate led to formation of uranium(v) and a decrease in pH. Upon interruption of photolysis, uranium(v) was seen to disproportionate. Yields of reduced uranium species were higher in degassed than aerated solutions, consistent with their oxidation by molecular oxygen in the latter case. Organic radicals were detected by electron paramagnetic resonance spectroscopy upon photolysis of cellulose acetate saturated with uranyl nitrate. The mechanism of photooxidation is suggested to involve hydrogen atom abstraction from the substrate by excited uranyl ions.

1 Introduction

The excited dioxouranium(vi) (uranyl) ion, UO_2^{2+} , is a powerful oxidant ($E^\circ = 2.6 \text{ V}$).^{1–4} Its photooxidation reactions have been extensively studied and a number of excellent reviews presented.^{1,2,5–10} A fairly detailed mechanistic understanding of these reactions is now available, with both electron-transfer and hydrogen atom-abstraction reactions occurring.^{1,10}

The interaction between the uranyl ion and polymers is of considerable importance in relation to the recovery and removal of this toxic cation from aqueous solutions.^{11,12} In addition, photolysis of polymers in the presence of uranyl ions may be of use both for polymer chain cleavage^{13,14} and photoinduced graft copolymerisation.^{5,15}

We have become interested in the interaction between cellulose derivatives and the uranyl ion. Whilst the photooxidation of various small carbohydrates by UO_2^{2+} has been known for a long time^{16,17} and reaction has been shown to proceed *via* formation of uranium(v),¹⁸ other mechanistic details are scarce. Upon photolysis of cotton wool saturated with uranyl perchlorate at 77 K, electron paramagnetic resonance (EPR) spectroscopy has revealed the presence of radicals which are thought to be formed from chain cleavage of cellulose.¹⁹ Valuable hints on possible mechanisms for these processes come from studies on the photooxidation of alcohols with the uranyl ion, where hydrogen atom abstraction appears to be the dominant mechanism with primary and secondary alcohols.^{10,20} In the case of tertiary alcohols, photooxidation is suggested to involve mainly electron transfer.^{10,19}

We report a study of the photooxidation of cellulose acetate by uranyl ions in both solution and a heterogeneous system. For comparison, we have also studied the photooxidation of the basic structural unit of this polymer, cellobiose (Fig. 1), by UO_2^{2+} .

2 Experimental

All reagents were of the purest grade commercially available and were used without further purification. β -D-Cellobiose was from Aldrich and cellulose acetate, with a 53.5–54.5% acetic

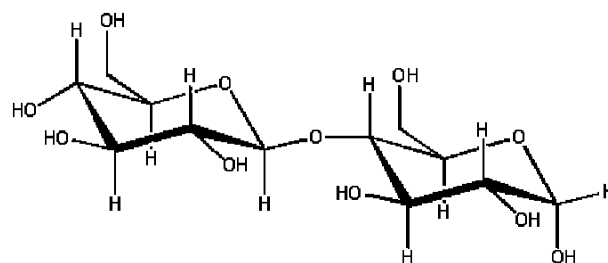


Fig. 1 The structure of cellobiose, the basic structural unit of cellulose.

acid content, was from BDH. Uranyl perchlorate was prepared by dissolving UO_3 in perchloric acid and the pH was adjusted with potassium hydroxide solution. Solutions were prepared in doubly distilled water or in pro-analysis grade acetone, either in equilibrium with air or deaerated by bubbling nitrogen through them for 30 min. pH values were adjusted by addition of dilute nitric acid.

Photolysis studies involved the use of a 125 W medium pressure mercury lamp with a glass filter (cut-off wavelength 320 nm) to minimise direct photolysis of the polymer. Viscosity measurements were carried out in aqueous solution using an Ostwald viscometer in a thermostat bath at 25 °C. The Mark–Houwink constants $K = 14.9 \times 10^{-3} \text{ g cm}^{-3}$ and $a = 0.82$ were used for solutions of cellulose acetate dissolved in acetone.²¹

Steady-state luminescence quenching studies were carried out using a Spex Fluorolog model 111 spectrometer. Samples were only irradiated when spectra were being recorded. Luminescence decays were measured with Applied Photophysics LKS 60 nanosecond flash photolysis apparatus using a frequency-tripled pulse ($\lambda = 355 \text{ nm}$) from a Quanta Ray GCR 130-01 Nd:YAG laser as the excitation source. Transient absorption spectra were recorded using a standard lamp source–monochromator–photomultiplier–oscilloscope set-up, as described in detail elsewhere.²² UV/visible absorption spectra were obtained using a Shimadzu UV-2100 spectrophotometer. EPR spectra were recorded with cellulose acetate samples at room temper-

ature on a Bruker ER 200D spectrometer at 9.55 GHz with a modulation field of 100 kHz. Samples were prepared by soaking in 0.1 or 0.01 M uranyl nitrate solutions and were dried initially in an oven at 85 °C, and subsequently under vacuum. Light from a filtered Xe–Hg lamp ($\lambda > 335$ nm) was used to irradiate samples directly in the EPR spectrometer cavity. Although no standard was used in these measurements, signals were in the region expected for typical organic polymer radicals.

3 Results

3.1 Quenching of UO_2^{2+} luminescence by cellulose acetate

The quenching of the luminescence of solutions of uranyl nitrate (0.1 M) in acetone by cellulose acetate was studied by steady-state measurements. Excitation of the above solutions with light of 337 nm leads to the well-characterised¹⁸ uranyl luminescence. As can be seen in Fig. 2, there is an increase in the luminescence intensity of the uranyl ion for the lower cellulose acetate concentration, but as the concentration of the quencher increases, the uranyl luminescence decreases. This might be due to the competition between complexation of the uranyl ion in the ground state by cellulose acetate and a dynamic quenching process involving cellulose acetate and excited uranyl ions. In the former case, the lifetime of the excited uranyl ion complex might be higher, hence the increase in the uranyl luminescence intensity for the lower cellulose acetate concentrations. Increasing the concentration of the quencher leads to a decrease in the uranyl luminescence intensity due to the quenching process involving cellulose acetate and the excited uranyl ion. Support for complexation in the ground state between uranyl ions and cellulose acetate comes from UV/visible absorption spectra, where slight changes in absorbance are observed in the presence of this quencher. The uranyl ion in acetone is present mainly as $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$,²³ and the observed spectral changes can best be interpreted in terms of complexation with cellulose acetate, since the UV/visible absorption spectra are known to be strongly dependent upon the equatorial coordination geometry of the complex.^{24,25} Only a slight increase in luminescence, with no change in band structure, was observed on leaving a cellulose acetate sample in uranyl nitrate solution in darkness for one week, indicating that dark reactions are not important.

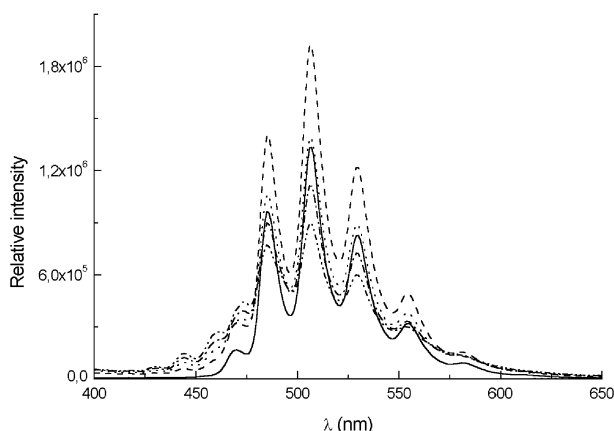


Fig. 2 Luminescence spectra of 0.1 M solutions of uranyl nitrate in acetone in the absence (—) and in the presence of 5 (---), 10 (···), 15 (-.-) and 20 (-.-.-) mg ml^{-1} cellulose acetate.

For the luminescence quenching region, Stern–Volmer behaviour was observed, as shown in Fig. 3. The steady-state Stern–Volmer constant determined from the plot is $K_{\text{SV}} = 0.0491 \text{ ml mg}^{-1}$.

3.2 Photolytic studies with cellulose acetate

Aerated solutions of uranyl nitrate (0.01 M) and cellulose acetate (10 mg ml^{-1}) in acetone were photolysed for 1 h. From viscometric studies, using a Mark–Houwink relationship, a

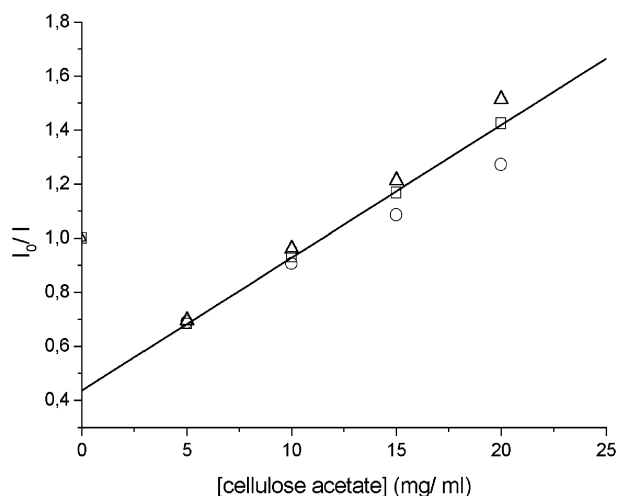


Fig. 3 Steady-state Stern–Volmer plots for the quenching of uranyl luminescence by cellulose acetate in acetone solution, with emission studied at 485 (○), 507 (△) and 530 nm (□).

value of 3.80×10^4 Da was calculated for the molecular mass of cellulose acetate before photolysis, whereas the value after photolysis was 3.21×10^4 Da. This result shows that photolysis proceeds with chain scission. However, in contrast with the behaviour in the case of sucrose,¹⁸ there was no evidence of the formation of U(IV) in the UV/visible absorption spectra of the photolysed solutions. Scission of the polymeric chain could occur by hydrogen atom abstraction,²⁶ with the formation of a polymer radical together with U(V), which would subsequently be expected to disproportionate.²⁷ However, when UO_2^{2+} is adsorbed in cellulose acetate,²⁸ the disproportionation of U(V) becomes less likely and its oxidation to U(VI) by oxygen is made easier.²⁹

The kinetics of chain scission were studied viscometrically. A sample was taken out every 5 min during a 75 min photolysis of an aerated solution of uranyl nitrate (0.05 M) and cellulose acetate (10 mg ml^{-1}) in acetone, the specific viscosity, η , of the solutions was determined and a plot of η vs. photolysis time is shown in Fig. 4. It can be seen that the specific viscosity decreases with photolysis time, in agreement with the idea that photolysis of cellulose acetate proceeds with chain scission.

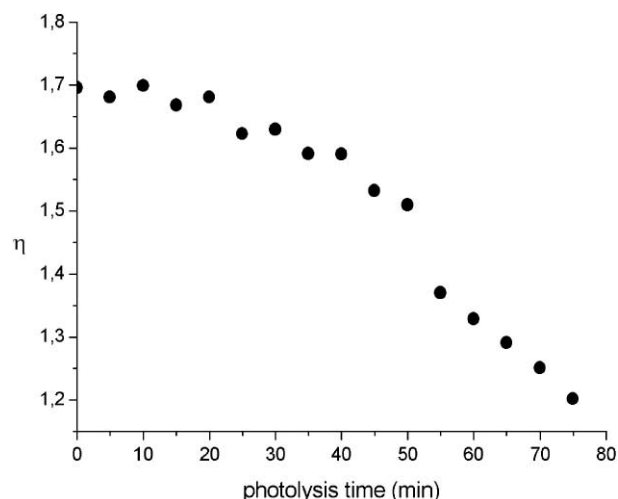


Fig. 4 Plot of specific viscosity (η) vs. photolysis time for an aerated solution of uranyl nitrate (0.05 M) and cellulose acetate (10 mg ml^{-1}) in acetone.

3.3 Model studies: quenching of the UO_2^{2+} excited state by cellobiose

To obtain further information on the mechanism of the quenching process, model studies were carried out using cellobiose as substrate. These were carried out in aqueous

Table 1 Bimolecular rate constants and Stern–Volmer constants for the quenching of $^*UO_2^{2+}$ by cellobiose

| pH | $k_0^a/10^5 \text{ s}^{-1}$ | $k_q^a/10^8 \text{ M}^{-1} \text{ s}^{-1}$ | $K_{SV}^b/10^2 \text{ M}^{-1}$ | $K_{SV}^c/10^2 \text{ M}^{-1}$ | $(K_{SV}/\tau)^d/10^8 \text{ M}^{-1} \text{ s}^{-1}$ |
|-----|-----------------------------|--|--------------------------------|--------------------------------|--|
| 1 | 7.03 | 1.58 | 2.24 | 4.53 | 3.04 |
| 2.5 | 6.42 | 1.44 | 2.24 | 3.71 | 2.35 |

^a Values obtained by linear regression of pseudo-first-order rate constants of $^*UO_2^{2+}$ decay as a function of cellobiose concentration. ^b Determined with $\lambda_{ex} = 355 \text{ nm}$ and $\lambda_{em} = 510 \text{ nm}$. ^c Steady-state values determined with $\lambda_{ex} = 337 \text{ nm}$ and $\lambda_{em} = 510 \text{ nm}$. ^d Using average lifetimes (τ) of 1.49 (pH 1) and 1.58 μs (pH 2.5), determined for $^*UO_2^{2+}$ in the absence of cellobiose.

solution, since the substrate is insoluble in acetone. Following excitation of aqueous solutions of uranyl nitrate (0.1 M, pH 2.5) with a frequency-tripled Nd:YAG laser pulse ($\lambda = 355 \text{ nm}$), a structured transient absorption was observed around 570 nm. This band is assigned to the well-characterised excited $^*UO_2^{2+}$ species,^{30,31} and the observed spectrum is presented as an inset in Fig. 5. The quenching of the luminescence of aqueous solutions of uranyl nitrate (0.1 M) by cellobiose (1×10^{-3} to $1.4 \times 10^{-2} \text{ M}$) was studied at the natural pH (pH 2.5) and at pH 1. Solutions were not degassed, as molecular oxygen does not affect excited uranyl ions.³² The decay of $^*UO_2^{2+}$ has been shown to be strongly dependent upon the medium, temperature, excitation intensity, *etc.*, and under some conditions is biexponential.^{20,33} This is probably associated with hydrolysis of the uranyl ion. However, at the relatively low pH and high uranyl concentration used in this study, literature data³⁴ indicate there is no significant formation of hydrolysed uranyl species, and the excited state refers to that derived from $[UO_2(H_2O)_5]^{2+}$.²³ Under these conditions, a monoexponential decay was considered for $^*UO_2^{2+}$. The decay was faster in the presence of cellobiose and obeyed the overall rate law

$$-\frac{d[{}^*UO_2^{2+}]}{dt} = (k_0 + k_q[\text{cellobiose}])[{}^*UO_2^{2+}]$$

Good linear plots of the pseudo-first-order rate constant as a function of cellobiose concentration were obtained at both pH values, from which values of k_0 and k_q were obtained (Table 1). Stern–Volmer plots for the quenching of the uranyl ion excited state by cellobiose are shown in Fig. 5. Steady-state data for the quenching of uranyl luminescence is also shown. The slopes for the steady-state data are higher than those corresponding to the excited-state decay data, as can be seen in Fig. 5, and the Stern–Volmer quenching constants (K_{SV}) in Table 1. The difference can be explained in terms of some static contribution to the

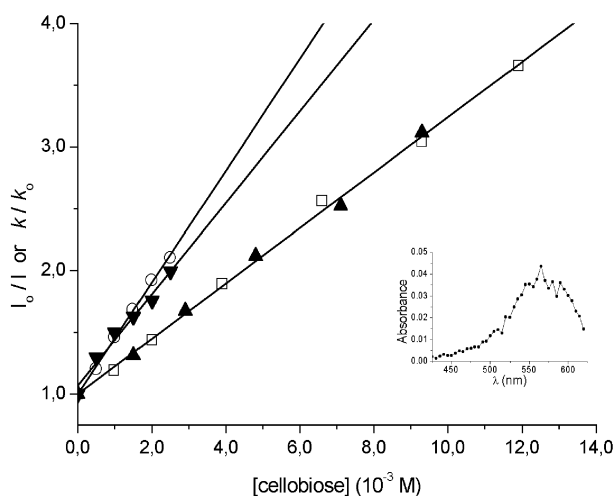


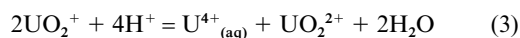
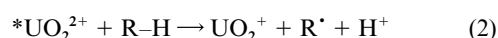
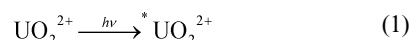
Fig. 5 Stern–Volmer plots for the quenching of the uranyl excited state by cellobiose in aqueous solution. Data shown are for the decay of uranyl luminescence at pH 1 (\square) and pH 2.5 (\blacktriangle), and steady-state data for the quenching of uranyl luminescence at pH 1 (\circ) and pH 2.5 (\blacktriangledown). Inset: the transient absorption spectrum observed after excitation of an aqueous solution of uranyl nitrate (0.1 M, pH 2.5) with a 355 nm laser pulse.

quenching, associated with complexation in the ground state of UO_2^{2+} by cellobiose. This provides further support for the suggested complexation between cellulose acetate and the uranyl ion. The Stern–Volmer quenching constants for the excited-state decay data are identical for both pH values, but differences are observed in the K_{SV} constants corresponding to the steady-state data for the two pH values. Excited-state decay data is not affected by complexation in the ground-state, whereas steady-state data has contributions from dynamic and static quenching. Depending on the pH, different dimeric and oligomeric uranium(vi) species are formed, although at pH 2.5, only around 5% of the uranyl ions are present as the hydrolysed species $(UO_2)_2(OH)_2^{2+}$.³⁵

3.4 Photolytic studies with cellobiose

Aerated and degassed aqueous solutions of uranyl nitrate (0.1 M) and cellobiose ($2.5 \times 10^{-3} \text{ M}$) were photolysed for 75 min; samples were removed every 15 min and their UV/visible absorption spectra recorded. Photolysis of the solutions lead to the appearance of new absorptions at $\lambda > 520 \text{ nm}$. However, the generation of the species giving rise to the observed spectra depends on the pH of the solution. Photolysis of a solution at pH 1 yields the spectrum of uranium(IV),¹⁸ with new absorptions around 550 and 650 nm (Fig. 6), whereas on photolysis of solutions at pH 2.5, the spectrum corresponds to that of uranium(V),^{36,37} with a new absorption band around 735 nm (Fig. 7). The band structure of the spectra are the same for aerated and degassed solutions, with the only difference being a slight change in the absorbance values. This will be explained below.

On photolysis, H atom abstraction from cellobiose by excited uranyl ions is expected to occur according to eqn. 2.^{10,20} UO_2^+ is stable only in a very narrow pH range (2–3) and is known to disproportionate *via* an acid-catalysed process (eqn. 3).^{27,37}



Thus, in the UV/visible absorption spectra recorded at pH 1 (Fig. 6), the absorption at 735 nm is not observed due to the disproportionation of UO_2^+ to U^{4+} and UO_2^{2+} . The results are consistent with photolysis initially producing uranium(V), which then disproportionates *via* an acid-catalysed reaction.

The absorbance at 735 nm, assigned to UO_2^+ , and the pH of the solutions were followed as a function of the time of irradiation, and plots are shown in Fig. 8. The absorbance at 735 nm increased rapidly, due to the formation of UO_2^+ , and there was a concurrent decrease in pH, due to the formation of H^+ (eqn. 2). When the irradiation was stopped for 2 h and the solutions kept in the dark, disproportionation of UO_2^+ occurred (eqn. 3), as evidenced by the decrease in the absorbance at 735 nm and the increase in pH of the solutions. When photolysis was reinitiated, the uranium(V) absorption at 735 nm and decrease in pH were again observed. This experiment was also performed with a solution of uranyl perchlorate (0.1 M) and cellobiose ($2.5 \times 10^{-3} \text{ M}$) to elucidate

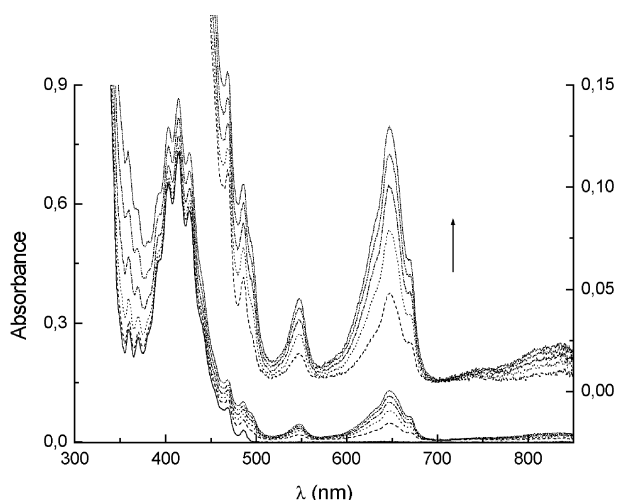


Fig. 6 UV/visible absorption spectra of degassed aqueous solutions of uranyl nitrate (0.1 M) and cellobiose (2.5×10^{-3} M) at pH 1, observed after 0, 15, 30, 45, 60 and 75 min photolysis.

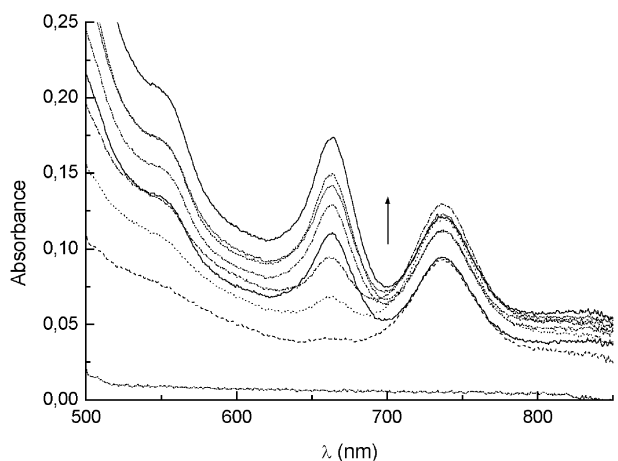


Fig. 7 UV/visible absorption spectra of aerated aqueous solutions of uranyl nitrate (0.1 M) and cellobiose (2.5×10^{-3} M) at pH 2.5, observed after 0, 30, 60, 90, 120, 150, 180, 210 and 270 min photolysis.

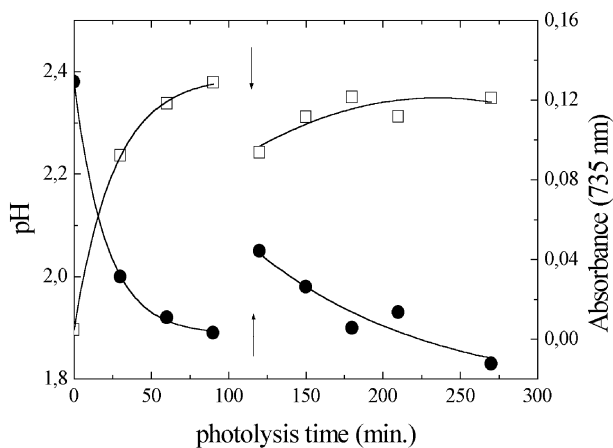
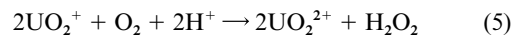
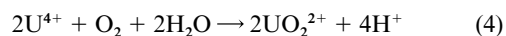


Fig. 8 Plots of pH (●) and uranium(v) absorbance at 735 nm (□) as a function of time of photolysis of an aerated aqueous solution of uranyl nitrate (0.1 M) and cellobiose (2.5×10^{-3} M) at pH 2.5. The arrows indicate when the point at which irradiation was stopped for 2 h.

the role of nitrate ions in the reaction pathway. Formation of uranium(v) was again observed, with absorbance values at 735 nm similar to those obtained with the uranyl nitrate solution, indicating that $^*UO_2^{2+}$, and not the nitrate ion, is oxidising cellobiose.

It was also observed that in the degassed solutions, the increase in the absorbance due to the U^{4+} and UO_2^+ species was

higher than in the corresponding aerated solutions. This can be readily explained by the presence of oxygen, which oxidises U^{4+} and UO_2^+ to UO_2^{2+} , according to the following reactions:^{29,38}



3.5 EPR studies

On photolysis of cellulose acetate saturated with an aqueous solution of uranyl nitrate (0.1 M) as a rigid medium at room temperature, an EPR signal was observed, as shown in Fig. 9. The spectra are shown after irradiation for 5 and 10 min, and 1 min after switching off the irradiation source. From the shape of the signal at different photolysis times, there appears to be more than one radical present. The observation of an EPR signal at room temperature and its maintenance after switching off the irradiation source indicates that the radicals formed are stable. The spectra are in a similar region to those previously reported for radicals from cellulose derivatives.³⁹ As with photolysis of uranyl salts adsorbed on pure cellulose,¹⁹ the radicals are probably formed by H atom abstraction from cellulose acetate by the excited uranyl ion.¹⁹ Non-selective hydrogen abstraction in cellulose,⁴⁰ cellulose acetate⁴¹ and cellobiose⁴¹ has previously been suggested on the basis of EPR spectra recorded both on direct UV irradiation and photosensitised experiments.

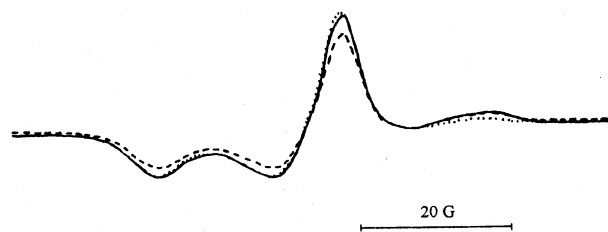


Fig. 9 EPR spectra observed on photolysis of a rigid matrix of uranyl nitrate (0.1 M) and cellulose acetate at room temperature after irradiation for 5 (---) and 10 (—) min, and 1 min after switching off the irradiation source (···).

4 Discussion

The decrease in the molecular mass of cellulose acetate, as followed by viscometric studies, after photolysis of solutions of uranyl nitrate and cellulose acetate in acetone clearly shows that photolysis proceeds with chain scission. Formation of stable radicals upon photolysis of a matrix of cellulose acetate and uranyl nitrate was observed by EPR spectroscopy. These radicals are most probably formed by H atom abstraction from the polymeric chain by the excited uranyl ion.¹⁹ However, reduction of the uranyl ion was not observed, *i.e.* there was no evidence of the formation of U(v) or U(IV) in the UV/visible absorption spectra of the photolysed solutions. This is probably due to the adsorption of the uranyl ions in the cellulose acetate, which makes the disproportionation of U(v) less likely and, hence, favours its oxidation to U(vi) by molecular oxygen.^{27,29} Literature data indicates a non-selective H atom abstraction from the polymeric chain, giving rise to different types of radicals.^{40,41}

Dynamic luminescence quenching studies of uranyl luminescence quenching by cellobiose have shown that this is a process involving a reaction between cellobiose and $^*UO_2^{2+}$. Steady-state luminescence measurements under identical conditions have shown that there is some static contribution to the quenching, associated with complexation in the ground state of UO_2^{2+} by cellobiose. A value of $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for the quenching rate constant (k_q). This value is greater than those reported in the literature for uranyl luminescence quenching by aliphatic alcohols ($k_q \approx 10^6 \text{ M}^{-1} \text{ s}^{-1}$),²⁰ but less than the values obtained for uranyl luminescence quenching by phenols ($k_q \approx$

$10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁴² indicating that cellobiose is a more effective quencher than aliphatic alcohols, where hydrogen abstraction is dominant,²⁰ and a less effective quencher than phenols, where the reaction is suggested to occur by electron transfer. These results are consistent with a reaction proceeding *via* hydrogen atom abstraction, but with the rate being enhanced both as a result of the larger number of accessible hydrogen atoms and electronic effects due to the carbohydrate rings.

Upon photolysis of uranyl nitrate and cellobiose solutions, new absorptions assigned to UO_2^+ and U^{4+} are observed in the UV/visible absorption spectra, with a concurrently decrease in pH. Again, these results support H atom abstraction from cellobiose by excited uranyl ions according to eqn. 2. While literature data⁴¹ suggest non-selective H atom abstraction from cellobiose, studies on various organic substrates⁴³ indicate hydrogen abstraction from secondary C–H bonds is more rapid than from CH_2 or OH groups. This suggests preferential attack at the hydrogen atoms bonded to the ring carbon atoms.

These studies indicate that photooxidation by the uranyl ion produces free radicals, and might provide a route to photo-initiated free radical graft copolymerisation of cellulose. Preliminary results support this proposition.

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