Initial Process of Photo-oxidation of Ethanol by Uranyl Ions in the Rigid Matrix at 77 K

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ESR spectra of radicals produced in the uranyl ion-photosensitized decomposition of ethanol have been measured in the rigid matrix at 77 K. At high concentrations of uranyl ions (>1 mol dm^{-3}), methyl radicals were observed. With decreasing concentrations of uranyl ions, $CH_3\dot{C}HOH$ radicals became important, as expected from the previous studies. This result suggests that the charge transfer mechanism is important in the ethanol rigid matrix, although the hydrogen atom abstraction mechanism is accepted as the main initial process.

The photochemistry of uranyl ions has been extensively investigated during the last fifty years.[1] In aqueous solutions, the quenching processes of the luminescence from excited uranyl ions by a variety of substrates were studied and several mechanisms have been proposed. In the case of alcohols, the quenching process is believed to occur through the intermolecular abstraction of a hydrogen atom by excited uranyl ions from a C–H bond of the hydroxylated carbon atom of alcohols.[2]

Liquid phase ESR studies using the spin-trapping method supported this mechanism.[3] All normal alcohol (RCH_2OH) used as substrates gave the alcohol radicals ($R\dot{C}HOH$) spin-trapped. In the case of secondary alcohols, the radicals produced by the loss of a hydrogen atom from the weakest C–H bond were observed; *i.e.*, $(CH_3)_2CHCH_2OH$ gave $(CH_3)_2\dot{C}CH_2OH$ and 2-propanol gave $(CH_3)_2\dot{C}OH$.

One exception was found with methanol. In this case, the principal radical spin-trapped was $CH_3O\cdot$ but not $\dot{C}H_2OH$. This reaction was classified as an exception due to an atypical behavior of methanol to uranyl ions.[1]

In the rigid matrix at low temperatures, a C–C bond cleavage was observed with secondary and tertiary alcohols.[4] For example, the photolysis of uranyl ions in a *t*-butyl alcohol glass gave the ESR spectrum of methyl radicals. This reaction was tentatively explained in terms of the charge transfer mechanism followed by the C–C bond cleavage:

$$(CH_3)_3COH + (UO_2^{2+})^* \rightarrow (CH_3)_3CO\cdot + UO_2^+ + H^+$$
$$(CH_3)_3CO\cdot \rightarrow (CH_3)_2CO + \cdot CH_3.$$

A similar observation was made with 1-propanol, for which ethyl radicals were found to be formed:

$$CH_3CH_2CH_2OH + (UO_2^{2+})^* \rightarrow CH_3CH_2CH_2O\cdot + UO_2^+ + H^+$$
$$CH_3CH_2CH_2O\cdot \rightarrow CH_2O + CH_3CH_2\cdot.$$

On the other hand, in the ethanol rigid matrix at 77K, the observed radicals were reported to be only $CH_3\dot{C}HOH$, suggesting that the abstraction of a hydrogen atom by excited uranyl ions from a C–H bond is the main process even in the matrix of ethanol as was found in the liquid phase.

Obviously there is some controversy in the mechanism of the photo-oxidation of alcohols by uranyl ions in the rigid matrix. We, therefore, have studied this reaction in some detail.

Experimental

The yellow crystalline powder of uranyl perchlorate, $UO_2(ClO_4)_2\cdot 7H_2O$, was prepared by the recrystallization from the perchloric acid solution of uranium trioxide, which was obtained by heating analytical grade $UO_2(NO_3)_2\cdot 6H_2O$ at 400 °C. Water, which was distilled after having been passed through an ion exchange resin column, was further refluxed with potassium permanganate and distilled twice. Ethanol (Wako Co.) was of guaranteed grade and used without further purification.

The observation of ESR spectra was made by means of a JEOL JES-FX3 spectrometer. A sample used for the ESR measurement was prepared by dissolving the $UO_2(ClO_4)_2\cdot 7H_2O$ powder in the known amount of ethanol or the mixture of the alcohol and water,and degassed under vacuum at the liquid nitrogen temperature. The yellow rigid glass thus obtained was irradiated with the light from a high-pressure mercury lamp (Ushio Electric Co.) through a filter (Corning 052) which cut off the wavelengths shorter than 365 nm. The ESR measurement was carried out during the light irradiation.

Results

When a 0.1 M (M=mol dm^{-3}) ethanol solution of $UO_2(ClO_4)_2\cdot 7H_2O$ was irradiated, the ESR spectrum, which appeared initially, was that of No. 5 spectrum shown in Fig. 1, and after a long irradiation, the spectrum changed to that of No. 6, together with an increase in the total intensity. This spectral change suggests that there are two kinds of radicals produced initially and their stabilities are not equal. Therefore, we measured the ESR spectra initially observed with the samples of various concentrations of $UO_2(ClO_4)_2\cdot 7H_2O$.

Figure 1 shows the results, where the numbers from 1 to 6 indicate the difference of the concentration of uranyl ions. All the spectra were obtained at 10 min from the start of light irradiation. No spectral change except the total intensity could be recognized during the first 10 min. The No. 1 spectrum clearly shows the presence of methyl radicals, while the No. 6 spectrum may be assigned to that of ethanol radicals ($CH_3\dot{C}HOH$).[5]

In order to investigate the stabilities of these radicals, the signal intensities were measured by turning off the lamp after a 30 min-irradiation. The intensity of the spectrum due to methyl radicals decayed to half in about 14 min, while the spectrum of $CH_3\dot{C}HOH$ radicals did not decay at all. This decay process

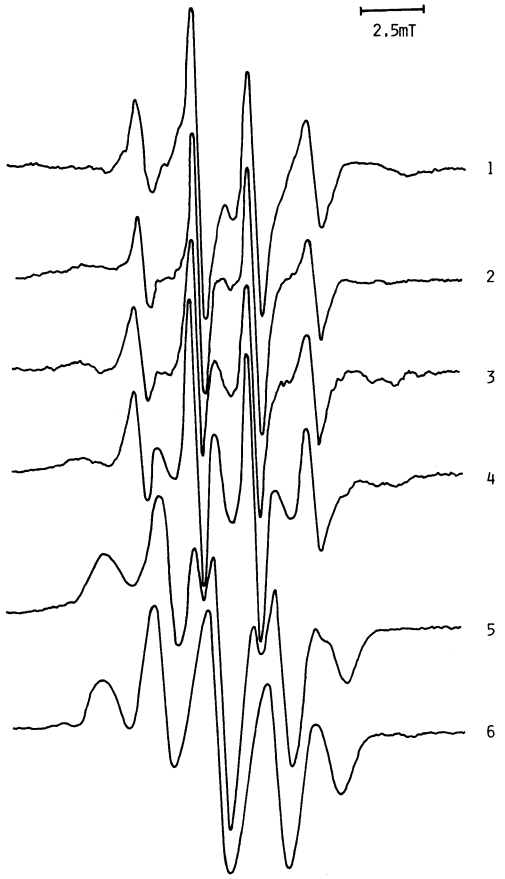

Fig. 1. ESR spectra of radicals initially produced in the uranyl ion-photosensitized decomposition of ethanol in the rigid matrix at 77 K. The numbers indicate the concentration of $UO_2(ClO_4)_2 \cdot 7H_2O$ in the matrix: 1, 2.5 M; 2, 1.8 M; 3, 1.0 M; 4, 0.5 M; 5, 0.1 M; 6, 0.04 M. Relative ESR intensities are arbitrarily adjusted.

was independent of both of the concentration of uranyl ions and the irradiation time.

Figure 2 shows the effect of the addition of water to the ethanol solution, where the concentration of uranyl ions was kept constant at 0.1 M (1 M=1 mol dm^{-3}). With the increase of water content, the ESR spectrum due to methyl radicals became more prominent than that due to $CH_3\dot{C}HOH$ radicals.

Discussion

According to the previous measurement on the ESR spectrum of the photolysis of uranyl ions in an ethanol rigid matrix, only $CH_3\dot{C}HOH$ radicals were observed,[4] but this measurement was carried out at low concentrations of uranyl ions (0.05—0.1 M); therefore, it is possible to overlook the spectrum due to methyl radicals initially produced. The present experiments clearly showed that methyl radicals are produced at the beginning of light irradiation.

The formation of methyl radicals may be explained in terms of the charge transfer mechanism followed by the C–C bond cleavage:

$$CH_3CH_2OH + (UO_2^{2+})^* \rightarrow CH_3CH_2O\cdot + UO_2^+ + H^+, \quad (1)$$

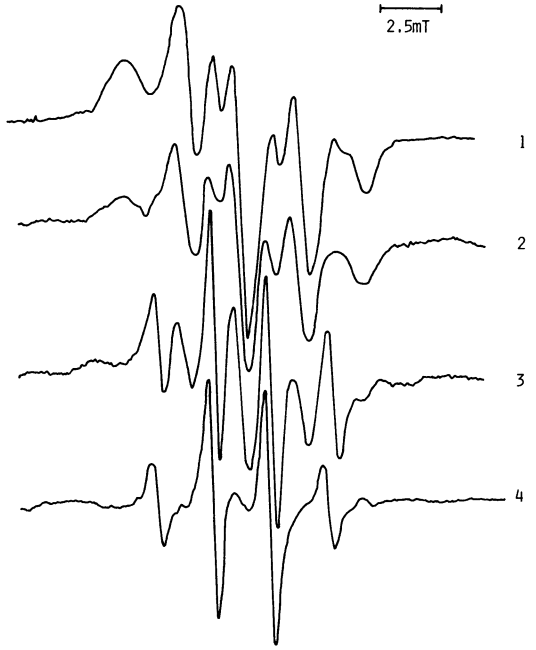

Fig. 2. ESR spectra of radicals produced in the uranyl ion-photosensitized decomposition of ethanol in the rigid matrix at 77 K. The numbers indicate the content of water: 1, no water added; 2, 20 volume % of water; 3, 50%; 4, 95%. The concentration of uranyl ions is kept constant at 0.1 M.

$$CH_3CH_2O\cdot \rightarrow \cdot CH_3 + CH_2O. \quad (2)$$

This is consistent with the mechanism proposed for the photosensitized decomposition of 1-propanol and secondary and tertiary alcohols in the rigid matrix at 77K.

For the formation of ethanol radicals ($CH_3\dot{C}HOH$) at lower concentrations of uranyl ions, we can consider three mechanisms: 1) the abstraction of a hydrogen atom by excited uranyl ions, 2) the abstraction of a hydrogen atom by ethoxyl radicals produced in Reaction 1 from the surrounding ethanol, and 3) the hydrogen atom abstraction by methyl radicals produced in Reaction 2.

The first mechanism may be discarded because, if this mechanism is operative, the formation of $CH_3\dot{C}HOH$ radicals should have been observed even at higher concentrations of uranyl ions. The third mechanism may also be disregarded since, if this is the case, the increase of $CH_3\dot{C}HOH$ radicals should have been observed with the decay of methyl radicals after the light irradiation was turned off.

It is well known that alkoxyl radicals are so reactive that the ESR spectra cannot easily be observed in the rigid matrix at 77 K;[6,7] therefore, if ethoxyl radicals are surrounded by ethanol, the abstraction of a hydrogen atom, Reaction 3, will occur immediately after the formation of ethoxyl radicals.

$$CH_5CH_2O\cdot + CH_3CH_2OH \rightarrow CH_3CH_2OH + CH_3\dot{C}HOH. \quad (3)$$

With the increase of uranyl ions, the concentration of free ethanol molecules from which the hydrogen atom is abstracted by ethoxyl radicals is concomitantly re-

duced, and Reaction 2 becomes more prominent than Reaction 3.

The decay of methyl radicals observed in the present experiments is probably due to the back reaction of UO_2^+ ions:

$$\cdot CH_3 + H^+ + UO_2^+ \rightarrow CH_4 + UO_2^+.$$

The Difference in Quenching Mechanism between Rigid Matrix and Liquid Phase. As has been discussed above, in the rigid matrices of alcohols at 77 K, the charge transfer mechanism seems to be the main process for the quenching of excited uranyl ions. On the other hand, the hydrogen atom abstraction mechanism is believed to be operative in the liquid phase photochemistry of uranyl ions.[1,8]

In the liquid phase, ethanol molecules surround an uranyl ion as shown in Fig. 3, and because of the

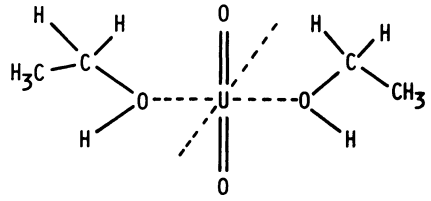

Fig. 3. The configuration of ethanol molecules around a uranyl ion in the liquid phase.

thermal vibration, an oxygen atom of the uranyl ion and a hydrogen atom of the C–H bond may occasionally approach each other very closely; therefore, when the excitation of uranyl ions occurs, the abstraction of a hydrogen atom may easily take place. On the other hand, in the rigid matrix at low temperatures, the ligand molecules will be mainly water, if $UO_2(ClO_4)_2 \cdot 7H_2O$ is used as the source of uranyl ions, since the heat of coordination is larger for water than for ethanol.[9] Consequently, the quenching of excited uranyl ions probably occurs through the hydrogen bond attached to an oxygen atom of the uranyl ion (Fig. 4). This process may be one detail of the charge transfer mechanism. A different approach is obviously necessary to establish these detailed mechanisms.

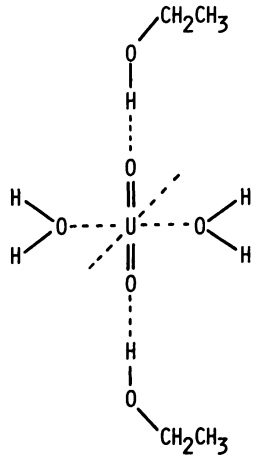

Fig. 4. The configuration of ethanol and water molecules around a uranyl ion in the rigid matrix at low temperatures.

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References

1) H. D. Burrows and T. J. Kemp, *Chem. Soc. Rev.*, **1974**, 139.
2) R. J. Hill, T. J. Kemp, D. M. Allen, and A. Cox, *J. Chem. Soc., Faraday Trans. 1*, **68**, 847 (1972).
3) A. Ledwith, P. J. Russel, and L. H. Sutcliffe, *Proc. R. Soc. London, Ser. A*, **332**, 151 (1973).
4) D. Greatorex, R. J. Hill, T. J. Kemp, and T. J. Stone, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2059 (1972).
5) D. Greatorex and T. J. Kemp, *Trans. Faraday Soc.*, **67**, 56 (1971).
6) W. A. Bernhard and D. M. Close, *J. Chem. Phys.*, **67**, 1211 (1977).
7) M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, **100**, 1964 (1978).
8) S. Sakuraba and M. Matsushima, *Bull. Chem. Soc. Jpn.*, **43**, 2359 (1970).
9) V. Gutman and R. Schmid, *Coord. Chem. Rev.*, **12**, 236 (1979).