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FORMATION OF BIACETYL IN THE PHOTOOXIDATION OF ACETALDEHYDE WITH THE URANYL ION

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In contrast to earlier reports of the formation of acetic acid, a deoxygenated aqueous acid solution containing 0.01 F uranyl ion and excess acetaldehyde gave biacetyl as the main organic oxidation product, upon irradiation with $\lambda \geqslant 3650$ Å from a 500-W high pressure mercury lamp, at 5∼15 °C.

It has been reported that the photooxidation of acetaldehyde with the uranyl ion in an aqueous acid solution led to the formation of the uranium(IV) species and acetic acid[1,2], where formation of the ground state complex between the organic substrate and the uranyl ion was assumed[2]. In sharp contrast to them, however, we have found the formation of biacetyl and not acetic acid as the main organic product in the photooxidation of acetaldehyde with the uranyl ion in an acid solution. A deoxygenated aqueous 0.5 N sulfuric acid solution containing 0.1 F uranyl ion and excess concentration of acetaldehyde gave the uranium(IV) species and the equimolar amount of biacetyl, upon irradiation with $\lambda \geqslant 3650$ Å using a glass filter from a 500-W high pressure mercury lamp, at 5∼15 °C. The amount of the uranium(IV) formed was estimated either by following its strong 650 nm absorbance or by the colorimetry with arsenazo-III[3], while the organic oxidation product was identified and determined by comparing its absorption and fluorescence spectra with the authentic sample (biacetyl), after extraction with ether or chloroform. A qualitative test involving conversion into a colored inner-complex nickel dioxime salt[4], also confirmed the formation of α-diketone. No other organic oxidation product was investigated since the molar ratio of the photoredox products, biacetyl/uranium(IV), was near unity (∼0.07 M for each product) to imply that only biacetyl was the main organic oxidation product.

Stern-Volmer relationship was obtained between the relative fluorescence intensity of the uranyl ion and the concentration of acetaldehyde.

The following mechanism, which is similar to that assumed for the photooxidation of alcohols by the uranyl ion[5], may be suggested.

$$(UO_2^{2+})^* + CH_3CH{=}O \longrightarrow UO_2^{+} + H^{+} + CH_3\dot{C}{=}O$$

$$2\ CH_3\dot{C}{=}O \longrightarrow CH_3COCOCH_3$$

$$2\ UO_2^{+} \xrightarrow[H^{+}]{} \text{U(IV) species} + UO_2^{2+}$$

It may be interesting to investigate the relationship between the photoreaction mechanism and the form of acetaldehyde in solution such as hydration and enolization, which needs further experiments.

Neither the uranium(IV) species nor biacetyl was detected in the dark at room temperature for 24 hours.

At present we can not understand the reason why the previous workers obtained acetic acid instead of biacetyl; the procedures for the qualitative analysis of the organic products has not been described$^{2)}$.

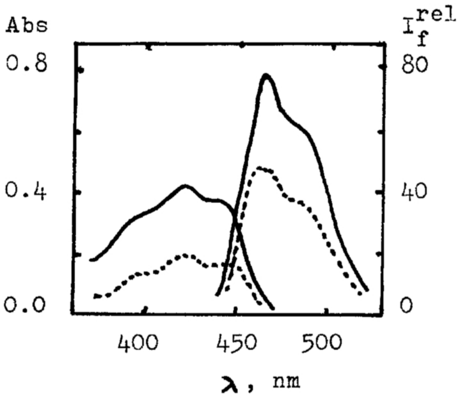

Fig. 1. Absorption (left) and fluorescence (right, uncorrected) spectra of the organic product in ether. Broken line: an ether solution of biacetyl extracted from an aqueous 0.1 N sulfuric acid solution containing 0.05 M biacetyl and 10 % acetaldehyde.

References

1) K. Venkatarao and M. Santappa, Current Sci. India, 33, 709 (1964); Chem. Abstr., 62, 4813 (1965).
2) K. Venkatarao and M. Santappa, Z. Physik. Chem. N. F., 54, 101 (1967).
3) H. Onishi and Y. Toita, Bunsekikagaku, 14, 1141 (1965).
4) F. Feigl and V. Anger, " Spot Tests in Organic Analysis", Elsevier, Amsterdam, 1966, pp. 328-329.
5) S. Sakuraba and R. Matsushima, Bull. Chem. Soc. Jap., 43, 2359 (1970); R. Matsushima and S. Sakuraba, J. Amer. Chem. Soc., 93, 5421 (1971).

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