Photo-oxidations of Acetoin and Biacetyl catalyzed by Tetrabutylammonium Decatungstate(4−) in Acetonitrile under Excess of Oxygen

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Under an excess of oxygen, the photo-oxidation of acetoin catalysed by $[NBu_4]_4[W_{10}O_{32}]$ and based on irradiation ($\lambda > 300$ nm) of the charge-transfer band in acetonitrile solution has been investigated. After irradiating for 30 h the products were biacetyl and acetic acid. The acetic acid was produced from both the acetoin and biacetyl. The rate constant for each path was determined by computer simulation. The production of biacetyl is based on dehydrogenation of acetoin in conjunction with the redox cycle of $[W_{10}O_{32}]^{4-}$ attained by reaction with O_2, whereas the production of acetic acid from biacetyl is based on the photoexcitation of biacetyl complexed with $[W_{10}O_{32}]^{4-}$ and subsequent reactions with O_2 and water.

Recently, interest has been taken in the catalytic photo-oxidation of organic substrates by various polyoxometalates in solution, where reoxidation of the reduced polyoxoanions is achieved either by reaction with O_2 or by evolution of H_2.[1–4] We have recently described the catalytic photo-oxidation of some secondary alcohols by $[W_{10}O_{32}]^{4-}$ under excess of O_2.[5,6] The oxidation of such substrates to ketones has been coupled with the photoreduction of $[W_{10}O_{32}]^{4-}$, and catalysis by the polyanion attributed to the redox cycle between the original oxidized form (pale yellow) and a two-electron reduced species (blue). Reoxidation of the reduced species is attained by reaction with O_2, where consumed O_2 is converted to water. The photo-oxidizability of $[W_{10}O_{32}]^{4-}$ has been understood as electron withdrawal from the substrate and subsequent dehydrogenation. In this work, we have found another type of oxidizability in the photo-oxidations of acetoin (3-hydroxybutan-2-one) and biacetyl (butane-2,3-dione) catalyzed by $[NBu_4]_4[W_{10}O_{32}]$ in CH_3CN solution under excess of O_2. Oxidation of biacetyl did not arise from the redox cycle of the decatungstate, but from photoexcitation of the complex formed between the polyanion and substrate.

Experimental

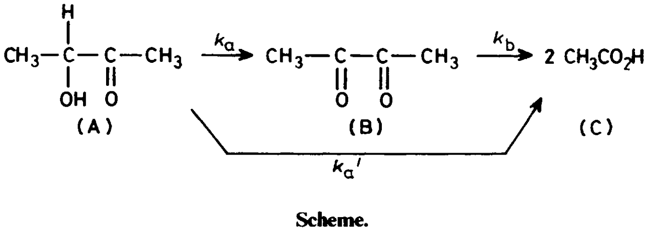
The materials, $[NBu_4]_4[W_{10}O_{32}]$[7] and $K_4[W_{10}O_{32}]\cdot 4H_2O$,[8] were prepared as previously described. Acetoin and biacetyl were obtained as 85% aqueous solutions (Wako Pure Chemical Industry Ltd.). All chemicals used were of analytical grade. The photoreaction was performed by irradiating ($\lambda > 300$ nm) a 75-cm^3 Pyrex flask containing a solution (50 cm^3) of decatungstate, organic substrate, and benzene as an internal reference for gas chromatography (g.c.). CH_3CN was used as a solvent for the $[NBu_4]^+$ salt of decatungstate and CH_3CN–water (1:1) (pH 2.5, H_2SO_4) for the K^+ salt. For the photoreaction under excess of oxygen, a *ca.* 5 000-cm^3 balloon filled with O_2 was attached to the Pyrex flask. A 75-W mercury lamp (SHL-100UV, Toshiba Corporation) in conjunction with a 5-cm cold water filter was used as a light source of external irradiation. Actinometry was performed by using hexan-2-one, resulting in a light intensity of 8.5×10^{-5} einstein h^{-1}. The changes in substrate and products were monitored by thermal conductivity detection gas chromatography (Shimadzu GC-8A) on a Porapak P column and also by ^1H and ^{13}C n.m.r. spectroscopy (JEOL GX-270).

Results and Discussion

By gas-chromatographic (g.c.) analysis, 5.8×10^{-2} mol dm^{-3} of biacetyl was detected after irradiating a CH_3CN solution (50 cm^3) containing $[NBu_4]_4[W_{10}O_{32}]$ (5×10^{-3} mol dm^{-3}), 85% aqueous acetoin (0.35 mol dm^{-3}) as a substrate, and benzene (0.128 mol dm^{-3}) as the internal reference, under excess of O_2 for 30 h. The amount of biacetyl produced corresponded to *ca.* 40% of the total substrate consumed. The residual 60% was acetic acid which was confirmed by ^1H and ^{13}C n.m.r., but not by g.c. analysis because of overlap with the peak of water under the conditions employed. Thus, in this photoreaction, the main product appeared to be acetic acid. The biacetyl produced corresponded to a 17% conversion of the substrate, the catalytic turn-over (ratio of the amount of product to the initial amount of $[W_{10}O_{32}]^{4-}$) was 12, and the quantum yield 1.1 mol einstein^{-1}. The decrease in acetoin could be treated approximately according to first-order kinetics and the rate constant was 8.8×10^{-6} s^{-1}.

A problem arose as to whether the acetic acid was produced from either acetoin or biacetyl, or from both. To clarify this point, a photoreaction with biacetyl as the substrate was studied. The irradiation was performed on a CH_3CN solution (50 cm^3) containing $[NBu_4]_4[W_{10}O_{32}]$ (5×10^{-3} mol dm^{-3}), 85% aqueous biacetyl (0.34 mol dm^{-3}), and benzene (0.128 mol dm^{-3}) under excess of O_2. It was observed that the substrate and oxygen were consumed during irradiation. The rate constant for decrease in biacetyl was estimated to be 1.8×10^{-6} s^{-1}.

For the photo-oxidation of acetoin (A) to biacetyl (B) and acetic acid (C), two processes can be considered; one is the stepwise path (I) $(A) \xrightarrow{k_a} (B) \xrightarrow{k_b} (C)$ and the other (II) contains the direct path $(A) \xrightarrow{k'_a} (C)$ in addition to path (I) (see Scheme). Using the two experimental rate constants obtained



Scheme.

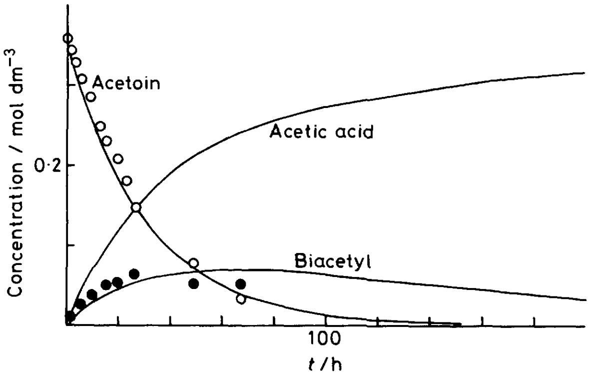


Figure. Calculated curves (full lines) and experimental data (circles) representing the concentration changes of substrate and products in the photo-oxidation of acetoin catalyzed by $[NBu_4]_4[W_{10}O_{32}]$ in CH_3CN solution under excess of O_2. Calculations were performed by using the rate constants $k_a + k_a'$ ($=8.8 \times 10^{-6}$ s^{-1}) and k_b ($=1.8 \times 10^{-6}$ s^{-1}), which were estimated experimentally, and by applying the ratio $k_a:k'_a:k_b = 3:7:2$ for the process (II). Open circles show acetoin as a substrate and filled circles biacetyl as one of the products

here (8.8×10^{-6} and 1.8×10^{-6} s^{-1}), computer simulation for (I) and (II) was attempted. The possibility of (I) was excluded, because the actual curve for biacetyl (B) produced deviated significantly from the calculated one. On the other hand, by changing the ratio of the rate constants k_a/k'_a in (II), we could simulate and obtain the best-fit ratio, $k_a:k'_a:k_b = 3:7:2$, which gave good agreement between the calculated and observed curves for (B) as depicted in the Figure. Here it should be noted that prolonged irradiation (>35 h) also leads to photo-oxidation of the $[NBu_4]^+$ counter ion, as recently described.[5] The computer analysis suggests that the acetic acid is produced more quickly from acetoin than from biacetyl. The oxidation of acetoin to biacetyl may be understood in terms of dehydrogenation of common secondary alcohols.[5,6] However, acetoin prefers the reaction path to acetic acid rather than the path to biacetyl. This is presumably related to the electron-withdrawing effect of the carbonyl adjacent to the OH group. In fact, we have recently described that photo-oxidation of ethyl lactate, a secondary alcohol with an adjacent carboxylic group, by $[NBu_4]_4[W_{10}O_{32}]$ could not be observed.[6] Moreover, in photo-oxidations with butane-2,3-diol as a substrate, the production of acetoin and its further oxidation products, biacetyl and acetic acid, were observed, but the direct path from butane-2,3-diol to acetic acid was not shown.

The production of acetic acid from biacetyl should be accompanied by C–C bond cleavage and oxygenation. This type of oxidation catalyzed by $[W_{10}O_{32}]^{4-}$ has not yet been reported. In conjunction with the redox cycle of $[W_{10}O_{32}]^{4-}$, we have examined the photoreaction of biacetyl. $K_4[W_{10}O_{32}]\cdot 4H_2O$ was used as a catalyst instead of $[NBu_4]^+$ salt to cut off the contribution from $[NBu_4]^+$ as a hydrogen source. The solution (50 cm^3) of the K^+ salt (5×10^{-3} mol dm^{-3}), 85% aqueous biacetyl (0.34 mol dm^{-3}), and benzene (0.128 mol dm^{-3}) in CH_3CN–water (1:1) (pH 2.5, H_2SO_4) was thoroughly deaerated and substituted with N_2. Despite irradiating for more than 24 h, the blue reduced species could not be obtained. This is in contrast to the irradiation of acetoin with $Y_4[W_{10}O_{32}]$ ($Y = [NBu_4]^+$ or K^+) under anaerobic conditions. This fact evidently excludes the possibility that the redox cycle between the reduced and oxidized forms of $[W_{10}O_{32}]^{4-}$ can participate in the photo-oxidation of biacetyl. By irradiating the solution resubstituted with excess of O_2, a decrease in substrate and consumption of O_2 were observed. The rate constant for the decrease in diacetyl was 1.3×10^{-6} s^{-1}. If the different media are taken into account, this value is comparable to that (1.8×10^{-6} s^{-1}) obtained in the catalysis by the $[NBu_4]^+$ salt. Oxidation did not take place in a blank system without the decatungstate. The possibility of thermal oxidation was also ruled out from experiments with the K^+ and $[NBu_4]^+$ salts in the dark. Thus, it is suggested that the oxidation of biacetyl does not proceed through the redox cycle of $[W_{10}O_{32}]^{4-}$, but through the photoexcitation of an appropriate complex formed between decatungstate and biacetyl. In this oxidation, O_2 should be an important participant, but not as a reoxidizing reagent for reduced polyanions as usually observed in the dehydrogenation of alcohols. Further, the water co-existent in the system should also take part in the production of acetic acid. Thus, the irradiation leads to photoexcitation of biacetyl complexed with $[W_{10}O_{32}]^{4-}$, but not the free biacetyl, resulting in C–C bond cleavage, insertion of O_2, and reaction with water.

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Received 11*th April* 1986; *Paper* 6/706