Substrate-selective Photo-oxidation of Benzyl Alcohol Derivatives with Oxygen, catalysed by an NAD$^+$ Model Compound

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An NAD$^+$ model compound, 10-methylacridinium ion (AcrH$^+$), catalyses the substrate-selective photo-oxidation of benzyl alcohol derivatives with oxygen in acetonitrile at 298 K, which is initiated by the electron-transfer reactions from benzyl alcohol derivatives to the singlet excited state of AcrH$^+$.

There have been extensive efforts to understand electron and proton flow in the reduction of various carbonyl compounds to alcohols by model compounds of reduced nicotinamide adenine dinucleotide (NADH),[1—3] an important coenzyme in biological redox reactions. However, little is known of the back reaction, *i.e.*, the conversion of alcohols into aldehydes by NAD$^+$ model compounds, which hitherto required base catalysis,[4] unusual NAD$^+$ model compounds being highly electron deficient,[5] or strongly electron-donating alcohols.[6] We report herein the efficient and selective conversion of benzyl alcohol derivatives into the corresponding aldehydes with oxygen under visible light irradiation (λ >390 nm), catalysed by 10-methylacridinium ion (AcrH$^+$) which has frequently been used as a simple NAD$^+$ model compound.[3]

Irradiation of an oxygen-saturated [^{2}H$_3$]acetonitrile solution containing AcrH$^+$ and benzyl alcohol or *p*-chlorobenzyl alcohol with visible light (λ >390 nm) resulted in the quantitative conversion (100 ± 3%) of the alcohols into aldehydes as shown in Figure 1. Without AcrH$^+$, the photochemical reaction did not proceed under otherwise identical conditions, and the AcrH$^+$ concentration remained constant during the photo-oxidation of alcohols in the presence of AcrH$^+$ (Figure 1). Thus, AcrH$^+$ acts as an efficient photocatalyst in the photo-oxidation of benzyl alcohol derivatives (X–C$_6$H$_4$CH$_2$OH) with oxygen [equation (1)]. The formation of hydrogen peroxide was confirmed by titration with iodide ion as described elsewhere.[7]

$$\text{X–C}_6\text{H}_4\text{CH}_2\text{OH} + \text{O}_2 \xrightarrow[\text{AcrH}^+]{h\nu} \text{X–C}_6\text{H}_4\text{CHO} + \text{H}_2\text{O}_2 \quad (1)$$

In the absence of oxygen, AcrH$^+$ was reduced by benzyl alcohol under visible light irradiation to yield protonated 10-methylacridan (AcrH$_3^+$) and benzaldehyde. However, once AcrH$^+$ is fully reduced to AcrH$_3^+$, the rate of oxidation of AcrH$_3^+$ by oxygen to regenerate AcrH$^+$ is very slow, compared with the efficient photocatalytic oxidation of benzyl alcohol with oxygen, catalysed by AcrH$^+$ (Figure 1). Thus, the reaction pathway for the AcrH$^+$ catalysed photo-oxidation may be different from that reported for the photo-oxidation of *p*-methylbenzyl alcohol with oxygen, catalysed by a flavin–Mg^{2+} complex, where a fully reduced flavin is readily oxidized by oxygen to regenerate an oxidized flavin.[7]

The quantum yields, Φ, of the photo-oxidation of various benzyl alcohol derivatives (X–C$_6$H$_4$CH$_2$OH) with oxygen,

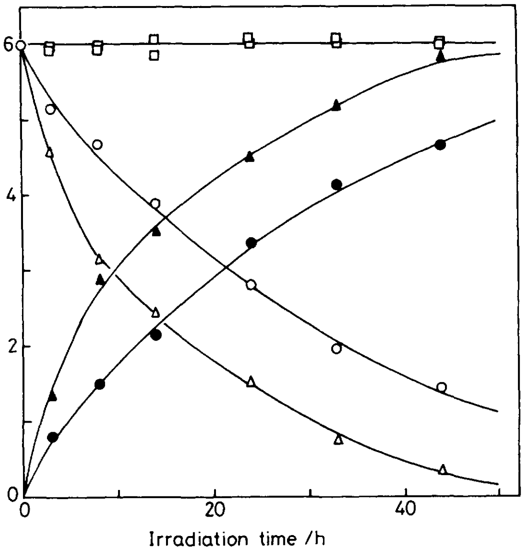
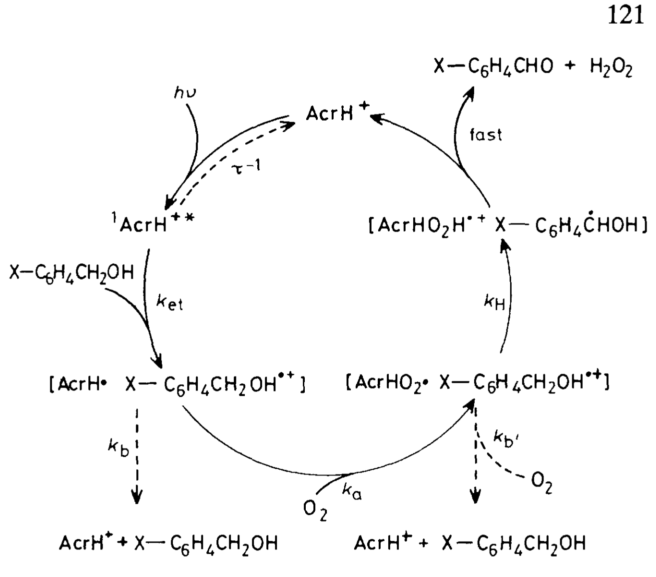


Figure 1. Photo-oxidation of $PhCH_2OH$ (○) or p-$ClC_6H_4CH_2OH$ (△) with oxygen, catalysed by $AcrH^+$ (□) under visible light irradiation (λ >390 nm), monitored by ^1H n.m.r. spectroscopy in CD_3CN at 298 K; $PhCHO$ (●), p-ClC_6H_4CHO (▲).

Table 1. Quantum yields Φ of photocatalytic oxidation of benzyl alcohol derivatives X–$C_6H_4CH_2OH$ (5.0×10^{-2} mol dm^{-3}) with oxygen, catalysed by $AcrH^+$, and rate constants of photoinduced electron-transfer reactions from X–$C_6H_4CH_2OH$ to $^1AcrH^{+*}$ in MeCN at 298 K.

X–$C_6H_4CH_2OH$, X	Φ^a	$\log(k_{et})^{b,c}$	$\log(k_q)^{b,d}$
p-HO	0	e	10.0
p-MeO	0	e	10.2
p-Pr^i	0.17	9.9	10.0
p-Me	0.09	9.9	10.1
p-Cl	0.14	8.0	8.3
H	0.07	7.6	7.8
p-NC	0	e	e
p-O_2N	0	e	e

[a] Determined from the initial rate of formation of X–C_6H_4CHO by using a ferrioxalate actiometer. [b] Units of k, dm^3 mol^{-1} s^{-1}. [c] Determined from plots of Φ^{-1} *vs.* $[X$–$C_6H_4CH_2OH]^{-1}$ using equation (2). [d] Determined from the fluorescence quenching of $^1AcrH^{+*}$ by X–$C_6H_4CH_2OH$. [e] Too small to be determined accurately.



Scheme 1

catalysed by $AcrH^+$ in MeCN at 298 K, were determined under conditions that both a ferrioxalate actinometer (0.15 mol dm^{-3}) and $AcrH^+$ absorb essentially all the incident light (>95%) from a Xenon lamp through a Toshiba UV-D36B filter transmitting light of $300 < \lambda < 420$ nm. The Φ values at a constant X–$C_6H_4CH_2OH$ concentration (5.0×10^{-2} mol dm^{-3}) are listed in Table 1. The maximum Φ value is achieved when X = p-Pr^i, whereas no photo-oxidation of X–$C_6H_4CH_2OH$ was observed with strongly electron-donating (X = p-HO or p-MeO) or -withdrawing (X = p-NC or p-O_2N) substituents (Table 1).

Such substrate-selective photocatalytic oxidation of X–$C_6H_4CH_2OH$ may be explained by Scheme 1, where the electron-transfer reaction from X–$C_6H_4CH_2OH$ to the singlet excited state of $AcrH^+$ produces X–$C_6H_4CH_2OH^{\bullet+}$ and $AcrH^\bullet$; the latter, a half-reduced radical $AcrH^\bullet$, is efficiently quenched by oxygen to give $AcrHO_2^\bullet$, and subsequent proton-transfer from X–$C_6H_4CH_2OH^{\bullet+}$ to $AcrHO_2^\bullet$ occurs, followed by electron- and proton-transfer in the cage to yield X–C_6H_4CHO and H_2O_2, regenerating $AcrH^+$. The strongly electron-withdrawing substituents on benzyl alcohol disfavour the electron-transfer process from X–$C_6H_4CH_2OH$ to $^1AcrH^{+*}$. In contrast, strongly electron-donating substituents favour the electron-transfer process, but disfavour the proton-transfer process from X–$C_6H_4CH_2OH^{\bullet+}$ to $AcrHO_2^\bullet$, since it is known that an increase in the electron-donor ability of substituents leads to a decrease in the proton-donor ability of the oxidized species.[8] Thus, in order to achieve efficient photocatalytic oxidation, both the electron- and proton-transfer processes should be fast enough to compete with the decay of $^1AcrH^{+*}$ and the back electron-transfer reaction from $AcrHO_2^\bullet$ to X–$C_6H_4CH_2OH^{\bullet+}$, respectively (Scheme 1); thus a sensitive balance between the electron- and proton-transfer processes to control the electron- and proton-donor abilities of X–$C_6H_4CH_2OH$ and X–$C_6H_4CH_2OH^{\bullet+}$, respectively, is required by choosing appropriate substituents X.

According to Scheme 1, the quantum yield Φ is given by equation (2), where $C = (k'_b + k_H)(k_b + k_a[O_2])/k_H k_a[O_2]$. Plots of Φ^{-1} *vs.* $[X$–$C_6H_4CH_2OH]^{-1}$ gave straight lines and from the slopes and intercepts the rate constants k_{et} of electron-transfer reactions from X–$C_6H_4CH_2OH$ to the excited state of $AcrH^+$ were determined using the lifetime of $^1AcrH^{+*}$ (τ 31 ns[9]). The fluorescence of $AcrH^+$ is known to be quenched by electron-transfer reactions with organic and inorganic electron-donors.[9] The quenching rate constants k_q of $^1AcrH^{+*}$ with X–$C_6H_4CH_2OH$ were determined from the slopes of the Stern–Volmer plots and the fluorescence lifetime (τ 31 ns[9]). Both the k_{et} and k_q values for various benzyl alcohol derivatives, thus determined, are also listed in Table 1, where the k_{et} values obtained from the dependence of Φ on the X–$C_6H_4CH_2OH$ concentration [equation (2)] based on

$$\Phi^{-1} = C[1 + (k_{et}\tau[X\text{–}C_6H_4CH_2OH])^{-1}] \qquad (2)$$

Scheme 1 agree well with the k_q values obtained directly from the electron-transfer quenching of the singlet excited state $^1AcrH^{+*}$ by X–$C_6H_4CH_2OH$. Such agreement is strong evidence that the photocatalytic oxidation of X–$C_6H_4CH_2OH$ is initiated by the photoinduced electron-transfer from X–$C_6H_4CH_2OH$ to $^1AcrH^{+*}$ (Scheme 1).

Received, 14th August 1986; Com. 1170

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