J. CHEM. SOC., CHEM. COMMUN., 1987

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 ($\lambda > 390$ 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 ($\lambda > 390$ 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–C₆H₄CH₂OH) with oxygen [equation (1)]. The formation of hydrogen peroxide was confirmed by titration with iodide ion as described elsewhere.⁷

$$X-C_6H_4CH_2OH + O_2 \xrightarrow{hv} X-C_6H_4CHO + H_2O_2$$
(1)

In the absence of oxygen, AcrH⁺ was reduced by benzyl alcohol under visible light irradiation to yield protonated 10-methylacridan (AcrH₃⁺) and benzaldehyde. However, once AcrH⁺ is fully reduced to AcrH₃⁺, the rate of oxidation of AcrH₃⁺ 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 of *p*-methylbenzyl alcohol with oxygen, catalysed by a flavin–Mg²⁺ 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-C₆H₄CH₂OH) with oxygen,



Figure 1. Photo-oxidation of PhCH₂OH (\bigcirc) or *p*-ClC₆H₄CH₂OH (\triangle) with oxygen, catalysed by AcrH⁺ (\square) under visible light irradiation ($\lambda > 390$ nm), monitored by ¹H n.m.r. spectroscopy in CD₃CN at 298 K; PhCHO (\bullet), *p*-ClC₆H₄CHO (\bullet).

Table 1. Quantum yields Φ of photocatalytic oxidation of benzyl alcohol derivatives X–C₆H₄CH₂OH (5.0 \times 10⁻² mol dm⁻³) with oxygen, catalysed by AcrH⁺, and rate constants of photoinduced electron-transfer reactions from X–C₆H₄CH₂OH to ¹AcrH^{+*} in MeCN at 298 K.

X–C ₆ H ₄ CH ₂ OH, X	Φ^{a}	$\log(k_{\rm et})^{\rm b,c}$	$\log(k_q)^{b,d}$
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-C₆H₄CHO by using a ferrioxalate actiometer. ^b Units of k, dm³ mol⁻¹ s⁻¹. ^c Determined from plots of Φ^{-1} vs. [X-C₆H₄CH₂OH]⁻¹ using equation (2). ^d Determined from the fluorescence quenching of ¹AcrH^{+*} by X-C₆H₄CH₂OH. ^e Too small to be determined accurately.

catalysed by AcrH⁺ in MeCN at 298 K, were determined under conditions such 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 < λ <420 nm. The Φ values at a constant X-C₆H₄CH₂OH concentration (5.0 × 10⁻² mol dm⁻³) are listed in Table 1. The maximum Φ value is achieved when X = p-Prⁱ, whereas no photo-oxidation of X-C₆H₄CH₂OH was observed with strongly electron-donating (X = p-HO or p-MeO) or -withdrawing (X = p-NC or p-O₂N) 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 $X-C_6H_4CH_2OH^{+}$ and



Scheme 1

AcrH·; the latter, a half-reduced radical AcrH·, is efficiently quenched by oxygen to give AcrHO2., and subsequent proton-transfer from X-C₆H₄CH₂OH⁺⁺ to AcrHO₂• occurs, followed by electron- and proton-transfer in the cage to yield X-C₆H₄CHO and H₂O₂, regenerating AcrH⁺. The strongly electron-withdrawing substituents on benzyl alcohol disfavour the electron-transfer process from X-C₆H₄CH₂OH to ¹AcrH^{+*}. In contrast, strongly electron-donating substituents favour the electron-transfer process, but disfavour the protontransfer process from X-C₆H₄CH₂OH⁺⁺ to AcrHO₂, 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 AcrHO₂ to X–C₆H₄CH₂OH $^{+}$, 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 $X-C_6H_4CH_2OH^{+}$, respectively, is required by choosing appropriate substituents X.

According to Scheme 1, the quantum yield Φ is given by equation (2), where $C = (k'_b + k_H) (k_b + k_a[O_2])/k_Hk_a[O_2]$. 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 ns⁹). 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 ns⁹). 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

$$\Phi^{-1} = C[1 + (k_{\rm et} \,\tau [\rm X-C_6H_4CH_2OH])^{-1}]$$
(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–C₆H₄CH₂OH. 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

References

- 1 U. Eisner and J. Kuthan, *Chem. Rev.*, 1972, **72**, 1; D. M. Stout and A. I. Meyers, *ibid.*, 1982, **82**, 223, and references therein.
- 2 B. W. Carlson and L. L. Miller, J. Am. Chem. Soc., 1985, 107, 479;
 M. F. Powell, and T. C. Bruice, *ibid.*, 1983, 105, 7139; S. Fukuzumi, N. Nishizawa, and T. Tanaka, J. Org. Chem., 1984, 49, 3571; J. Chem. Soc., Perkin Trans. 2, 1985, 371.
- A. Ohno, T. Shio, H. Yamamoto, and S. Oka, J. Am. Chem. Soc., 1981, 103, 2045; M. M. Kreevoy and I.-S. H. Lee, *ibid.*, 1984, 106, 2550; A. K. Colter, G. Saito, F. J. Sharom, and A. P. Hong, *ibid.*, 1976, 98, 7833; S. Fukuzumi, M. Ishikawa, and T. Tanaka,

- J. Chem. Soc., Chem. Commun., 1985, 1069; Tetrahedron, 1986, 42, 1021.
- 4 S. Shinkai, H. Era, T. Tsuno, and O. Manabe, Bull. Chem. Soc. Jpn., 1984, 57, 1435; A. Ohno, S. Ushida, and S. Oka, Tetrahedron Lett., 1982, 23, 2784.
- 5 K. Wallenfels and W. Hanstein, Angew. Chem., Int. Ed. Engl., 1965, 4, 867; F. Yoneda, H. Yamato, and M. Ono, J. Am. Chem. Soc., 1981, 103, 5943.
- 6 S. Shinkai, T. Tsuno, and O. Manabe, J. Chem. Soc., Perkin Trans. 2, 1984, 661.
- 7 S. Fukuzumi, K. Kuroda, and T. Tanaka, J. Am. Chem. Soc., 1985, 107, 3020.
- 8 C. J. Schlesener, C. Amatore, and J. K. Kochi, J. Am. Chem. Soc., 1984, **106**, 7472; A. Martin, P. Nicholas, and D. R. Arnold, Can. J. Chem., 1982, **60**, 2165.
- 9 H. Gebert, W. Regenstein, J. Bending, and D. Kreysig, Z. Phys. Chem., Leipzig., 1982, 263, 65; A. T. Poulos, G. S. Hammond, and M. E. Burton, Photochem. Photobiol., 1981, 34, 169.