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Structure–reactivity correlation for the ligand-decelerated catalytic osmium tetraoxide dihydroxylation of alkenes

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ABSTRACT: Kinetic studies on the ligand-decelerated catalytic OsO_4 dihydroxylation of seven substituted styrenes with trimethylamine-*N*-oxide in the absence and in the presence of pyridine ligand have been carried out. The rates correlate with the Hammett relationship and V-shaped plots with a maximum are in agreement with the oxidation of osmate(VI) ester in the rate-determining step. Copyright © 2002 John Wiley & Sons, Ltd.

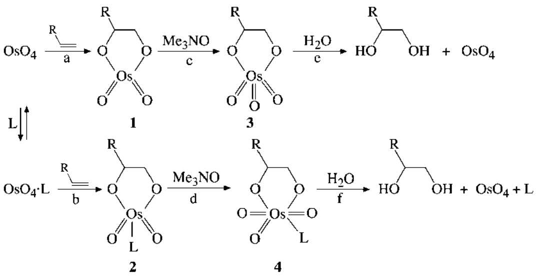
KEYWORDS: ligand-decelerated catalysis; osmium tetraoxide dihydroxylation; V-shaped Hammett plot

INTRODUCTION

As a part of our continuing investigations into the *tert*-amine-decelerated catalytic OsO_4 dihydroxylation of alkenes with trimethylamine-*N*-oxide (Me_3NO) as a secondary oxidant,[1,2] we have also examined the alkene substituent effects on the reaction rate by examining the Hammett plot.

There have been several kinetic and mechanistic studies of plain hydroxylation[1–8] and Sharpless's asymmetric dihydroxylation of alkenes[9–13] by either stoichiometric OsO_4 oxidation[3,5–7,12,13] or by catalytic OsO_4 oxidation using a secondary oxidant.[1,2,4,9–11] Ligand-accelerated catalysis[14] has long been recognized in the presence of *tert*-amines[5,7,8,15,16] and chiral alkaloids as ligands.[7,8,12,13,17] Sharpless and coworkers reported that the rate-determining step consists of the osmylation reaction forming dioxomonoglycolatoosmium(VI) ester (**1**) and their *tert*-amine adducts (**2**) with only a single amine participation[9–12] (Scheme 1, steps a and b) and rate saturation occurs at high amine concentrations.[9,10,12] Sharpless's cycle for catalytic OsO_4 dihydroxylation of alkenes is well established.[11] For the formation of Os(VI) esters **1** and **2** the currently favored [3 + 2] mechanism[18–20] has recently received more additional support from theoretical studies[21] compared with the [2 + 2] mechanism involving formation of an osmaoxetane via an alkene complex.[22,23]

Our long-term kinetic studies[1,2] led to a rate law that is first-order in OsO_4, first-order in Me_3NO and zeroth-order in alkene, and thus the rate-determining step is the oxidation of the relatively substitution-inert dioxomonoglycolatoosmium(VI) esters **1** and their monoamine adducts **2** to substitution-labile trioxomonoglycolatoosmium(VIII) esters **3** and **4** by Me_3NO (Scheme 1, steps c and d). All *tert*-amines have been found to retard the catalysis greatly, with an inverse first-order or partial order, and beyond a definite concentration of amine the rate reaches a minimum and remains constant.



Scheme 1

RESULTS AND DISCUSSION

Our aim was to investigate the electronic effects of alkenes in some detail in the ligand-decelerated catalytic OsO_4 dihydroxylation with Me_3NO in order to gain some insight into the rate-determining step, and we used dihydroxylation of substituted styrenes in the absence and presence of pyridine as a probe for Hammett plots.

tert-Amine oxides oxidize by atom and electron transfer.[24] In the atom transfer reaction, the atom being oxidized and the atom being reduced form directed bonds to a common atom, which then serves as a bridge for

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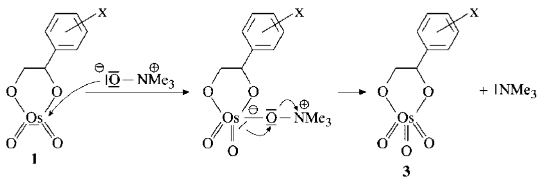

Scheme 2

electron transfer (Scheme 2). In this case the rate is strongly dependent on the nature of the bridge, i.e. on the affinity of the reductant for the bridging group.[25] The substitution on the alkene can change the affinity of Os(VI) both toward the oxygen transfer, to form an intermediate complex, and the electron transfer, to form Os(VIII)=O.

By testing the Hammett relationship in the ligand-decelerated catalytic OsO_4 dihydroxylation of substituted styrenes with Me_3NO we hoped to be able to determine both the effect of the Os(VI) ester structure and the presence of ligand on the ease and mechanism of oxygen transfer in the rate-limiting oxidation step.

If oxidation of Os(VI) ester **1** to Os(VIII) ester **3** with Me_3NO is a two-step reaction, i.e. Os–O—NMe_3 complex formation in the first step and O—N bond cleavage in the second step, the two steps respond differently to substituents at the test site. We would then expect that both electron-withdrawing and electron-donating substituents will facilitate the reaction: the less electron density that is pushed on the osmium by an electron-withdrawing substituent results in the rate increase in the formation of the complex whereas the more electron density that is pushed on the osmium by an electron-donating substituent results in a rate decrease in the breakdown of the complex. Thus, we would expect this to result in the formation of V-shaped Hammett plots.[26–28] If, however, the electron donation step is slow the reaction will be facilitated with only electron-withdrawing substituents, resulting in a linear Hammett plot with a positive slope.

Electronic effects in *tert*-amine-accelerated dihydroxylation of alkenes have been investigated thoroughly by Sharpless and coworkers.[29] The negative reaction constant of a Hammett plot based on the kinetics of the stoichiometric dihydroxylation of substituted styrenes is consistent with the electrophilic character of OsO_4 in the rate-limiting osmylation step and agrees with the observations on symmetrical *trans*-stilbenes[30] and substituted vinyl ethers.[31] However, *tert*-amine-accelerated reactions were found to be faster for styrenes bearing either electron-donating or electron-withdrawing substituents, resulting in curved Hammet plots with a minimum.

Since it is generally accepted that the existence of a Hammett plot requires that the reaction series under study be either isoenthalpic, isoentropic or isokinetic,[26,27] it is noteworthy that we observed the same mechanism in the ligand-decelerated OsO_4 dihydroxylation of substituted styrenes, which is consistent with the proposed kinetic law;[2] we also found that a linear relationship exists between $\Delta H‡$ and $\Delta S‡$ values in the reaction of a model substitued styrene in the presence of varying ligand concentration, implying the same mechanism in the absence and in the presence of a ligand.[32]

Table 1. Second-order rate constants of catalytic OsO_4 dihydroxylation of substituted styrenes X—$C_6H_4CH{=}CH_2$ with Me_3NO in *tert*-butyl alcohol at 50 °C in the absence and in the presence of pyridine[a]

	k_2 (M^{-1} s^{-1})	
X	without pyridine	presence of pyridine
H	2.40	1.20
4-CH_3	2.77	1.19
4-$ClCH_2$[b]	3.08	1.36
4-CH_3O	2.15	0.53
4-Cl	3.30	1.94
4-CF_3	0.86	0.20
3-Cl	1.35	0.53
3-Br	1.07	0.41

[a] [alkene] = 0.436 M; [Me_3NO] = 0.451 M; [OsO_4] = 1.2×10^{-3} M; [pyridine] = 10×10^{-3} M.
[b] Blank experiments show that no observable solvolysis of benzylic chloride takes place.

Second-order rate constants in the catalytic OsO_4 dihydroxylation of substituted styrenes with Me_3NO in *tert*-butyl alcohol at 50 °C in the absence and in the presence of pyridine are summarized in Table 1 and Hammett plots for the reactions using σ valves[28,33,34] are given in Figure 1.

The Hammett plots for reactions both in the absence and presence of pyridine are V-shaped plots with a maximum and show two distinct lines for each of which there is a good correlation between the σ values and the logarithm of the rate constants. Electron-donating groups fall on the one side with positive slopes and electron-withdrawing groups on the other side with negative slopes. The break in each plot corresponds to *p*-chlorostyrene. Reaction constants ρ were found to be $+0.32 \pm 0.04$ ($r = 0.858$) and -1.89 ± 0.10 ($r = 0.952$) in the absence of pyridine and $+0.93 \pm 0.02$ ($r = 0.914$) and -3.34 ± 0.11 ($r = 0.963$) in the presence of pyridine. Thus, as expected, V-shaped Hammett plots provide strong support for the concerted mechanism of the rate-determining oxidation step that we proposed for ligand-decelerated catalytic OsO_4 dihydroxylation of alkenes. The degree of concertedness is expected to depend on the substituent effects.

In addition, the rate decrease with electron-donating substituents requires development of a negative charge or increase in the negative charge in the rate-determining step. The formation of the intermediate complex by electron donation from *tert*-amine oxide oxygen to osmium supports this fact, resulting in a positive ρ.

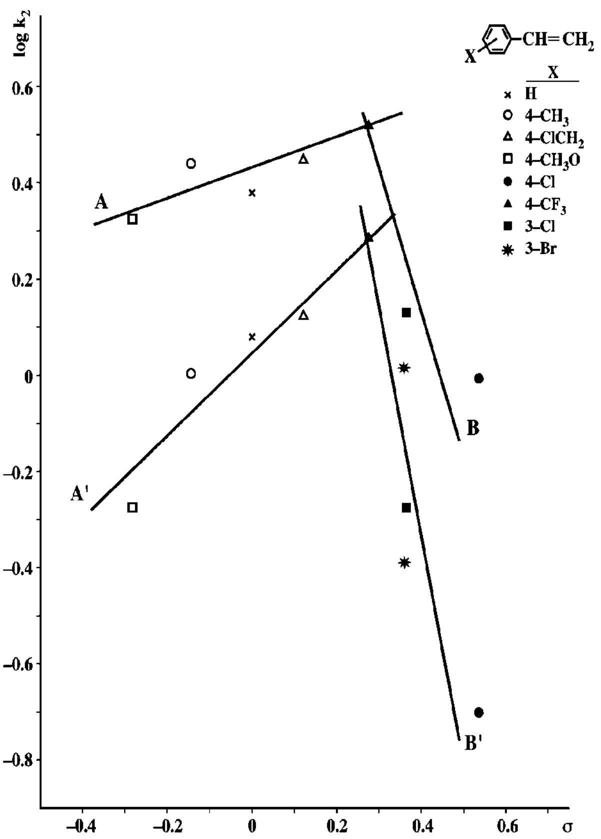

Figure 1. Hammett plots for second-order rate constants k_2 using σ values. A and B: in the absence of pyridine; A′ and B′: in the presence of pyridine

The higher reaction constants show the susceptibility of the pyridine-decelerated reaction to the effects exerted by the substituent. This result is as should be expected from the above fact. The rate decrease with electron-donating substituents is higher in the presence of a ligand than that without a ligand, since negative charge on osmium will be hardly dispersed in the coordination of ligand. However, electron-withdrawing substituents will be more effective in the presence of a ligand at dispersing the negative charge on osmium.

In conclusion, we have shown that the Hammett relationship for the catalytic OsO_4 dihydroxylation of alkenes with Me_3NO in *tert*-butyl alcohol in the absence and in the presence of a *tert*-amine ligand gives V-shaped plots with a maximum. This finding is consistent with the oxidation of osmate(VI) ester in the rate-determining step of ligand-decelerated catalytic OsO_4 dihydroxylation.

EXPERIMENTAL

tert-Butyl alcohol was fractionated. Osmium tetraoxide (CAUTION: very toxic) and Me_3NO were obtained from Aldrich Chemical Co. Alkenes were obtained from various sources and purified according to the published procedures. The kinetics of catalytic OsO_4 dihydroxylation of alkenes with Me_3NO in *tert*-butyl alcohol at 50.0 °C were followed by measuring the concentration of the remaining alkene by gas chromatography as previously described.[1,2] The data were taken with almost equal concentrations of alkene and Me_3NO under limiting OsO_4 concentrations, i.e. $[\text{alkene}] = 0.436$ M, $[Me_3NO] = 0.451$ M, $[OsO_4] = 1.20 \times 10^{-3}$ M. The observed pseudo first-order rate constants k_1 were calculated from the slopes of the linear plots of log c_t versus time, where c_t is the concentration of alkene at time t. First-order plots proved linear over three half-lives. Each kinetic run ordinarily utilized 10–12 points to obtain the rate data. Reproducibility was generally ±3%. Rate constants k_2 were calculated as $k_1/[OsO_4]$. Measurements were also made in the presence of 10×10^{-3} M pyridine.

Rate constants and reaction constants of the Hammett plots were obtained by using a linear least-squares program on a computer.

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