

Ligand Effects on the Redox Chemistry of Oxo(phosphine)ruthenium(IV) Complexes: Oxidation of Alcohols

James G. Muller, John Henry Acquaye, and Kenneth J. Takeuchi*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received April 23, 1992

Oxoruthenium complexes which contain para-substituted triphenylphosphine ligands cleanly oxidize para-substituted benzyl alcohols to the corresponding benzaldehydes. Linear free energy correlations between the logarithms of the second-order rate constants of benzyl alcohol oxidation and either the potential values of the ruthenium(IV)/ruthenium(III) redox couples of the oxoruthenium complexes or the Hammett σ values of the substituents of the para-substituted triphenylphosphine ligands were observed. However, there were no good correlations for plots of $\log(k_X/k_H)$ versus the Hammett substituent constants σ , σ^+ , or σ^- for the oxidation of the para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})\text{PPh}_3](\text{ClO}_4)_2$. Notably, the plot of $\log(k_X/k_H) - \sigma^+$ versus σ^- , where σ^+ is the free radical stabilization constant, gave an excellent correlation with $\rho = -0.57$ and $R^2 = 0.99$ for the oxidation of the para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})\text{PPh}_3](\text{ClO}_4)_2$ in methylene chloride. From these and other results, we propose a reaction pathway for the oxidation of benzyl alcohol by oxoruthenium(IV) complexes which involves a partial hydrogen atom abstraction from the benzylic carbon in the rate-determining step.

Introduction

The ability to oxidize alcohols, in particular benzylic and secondary alcohols, to the corresponding aldehydes or ketones without further oxidation to carboxylic acids is an important synthetic process.¹⁻⁸ The reagents commonly used for selective alcohol oxidation often utilize toxic metals such as chromium, employ high temperatures, strong acids, or strong bases, and suffer from poor selectivity and low product yield.^{1,5,7,8} Thus, there has been considerable attention focused on the development and study of novel oxidants that will selectively oxidize alcohols.¹⁻¹¹

Owing to the importance of alcohol oxidation there is a need to develop novel oxidation reagents that will act as selective oxidants and can also be synthetically modified. In this manner, the redox reactivity of the reagents can be rationally varied, and established mechanistic probes can be applied to investigate the mechanisms of alcohol oxidation reactions. The use of oxoruthenium complexes for the selective oxidation of alcohols is intriguing, since oxoruthenium complexes containing tertiary phosphine ligands act as potent stoichiometric and catalytic oxidants under mild conditions.¹²⁻¹⁶ In addition, the tertiary phosphine ligand provides steric, electronic, and hydrophobic control of the oxoruthenium center.^{13,14} Specifically, the use of para-substituted triphenyl phosphine ligands allows for the

electronic modification of the oxo(phosphine)ruthenium(IV) complexes while maintaining constant steric properties,¹⁷ thereby producing a method of controlling the rate of substrate oxidation and allowing the use of linear free energy relationships for the correlation of electronic properties to the rate constants of alcohol oxidation.

Linear free energy relationships have been utilized in a number of studies involving organic substrate oxidations with transition metal oxidants in which the organic substrate is modified.^{3,18-25} Even though electronic modifications of transition metal complexes have been utilized to control reaction rates and study the mechanisms associated with a variety of metal centered reactions,²⁶ there are only a few examples of reactions involving organic substrate oxidation by transition metal complexes containing an oxo ligand.^{20,25}

With this paper, we wish to report the kinetics and mechanistic investigation of the oxidation of benzyl alcohol and para-substituted benzyl alcohols by a series of $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes (where $\text{bpy} = 2,2'$ -bipyridine and $\text{P}(p\text{-C}_6\text{H}_4\text{X})_3 =$ para-substituted triphenyl phosphine ligand). The use of para-substituted triphenylphosphine ligands allows for control of the potential values of the ruthenium(IV)/(III) redox couples of the oxo(phosphine)ruthenium(IV) complexes while maintaining a constant cone angle of the phosphine ligand. In addition, by including in this discussion kinetic data involving the oxidation of a variety of alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$, this paper represents a rare example in which the rate constants for benzyl alcohol oxidation are interpreted in terms of both substrate electronic properties and oxidant electronic properties. From our studies, we propose a reaction pathway

- (1) Sasson, Y.; Wiener, H.; Bashir, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1574.
- (2) Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1625.
- (3) Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 120.
- (4) Moodie, R. B.; Richards, S. N.; Thorne, M. P. *J. Chem. Soc., Chem. Commun.* **1987**, 870.
- (5) Audette, R. J.; Quail, J. W.; Smith, P. J. *Tetrahedron Lett.* **1971**, 279.
- (6) Futami, Y.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3567.
- (7) Hirano, M.; Morimoto, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 4069.
- (8) Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1989**, 519.
- (9) Yoneda, F.; Tanaka, K.; Yamato, H.; Moriyama, K.; Nagamatsu, T. *J. Am. Chem. Soc.* **1989**, *111*, 9199.
- (10) Wong, K.; Che, C.; Anson, F. C. *Inorg. Chem.* **1987**, *26*, 737.
- (11) Meyer, T. J.; Roecker, L. *J. Am. Chem. Soc.* **1987**, *109*, 746.
- (12) Marmion, M. E.; Takeuchi, K. *J. Am. Chem. Soc.* **1986**, *108*, 510.
- (13) Marmion, M. E.; Takeuchi, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1396.
- (14) Marmion, M. E.; Takeuchi, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2385.
- (15) Leising, R. A.; Takeuchi, K. *J. Inorg. Chem.* **1987**, *26*, 4391.
- (16) Marmion, M. E.; Takeuchi, K. *J. Am. Chem. Soc.* **1988**, *110*, 1472.

- (17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
- (18) Neumann, R.; Abu-Gnim, C. *J. Am. Chem. Soc.* **1990**, *112*, 6025.
- (19) Garrison, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 191.
- (20) Garrison, J. M.; Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960.
- (21) Shibagaki, M.; Kuno, H.; Takahashi, K.; Matsushita, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4153.
- (22) Kinnear, J. F.; Albert, J. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 6124.
- (23) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1989**, *108*, 507.
- (24) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
- (25) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.
- (26) For a review, see: Senoff, C. V. *Coord. Chem. Rev.* **1980**, *32*, 111.

which involves a partial hydrogen atom abstraction in the transition state followed by a rapid reaction of the Ru(III)-OH intermediate and the strongly reducing alcohol radical intermediate to form the final products.

Experimental Section

Materials. The following chemicals were obtained commercially and used as received: ruthenium trichloride trihydrate (Johnson Matthey), 2,2'-bipyridine (Aldrich Chemical Co.), triphenylphosphine (Aldrich Chemical Co.), tris(*p*-methoxyphenyl)phosphine (Strem Chemicals, Inc.), tris(*p*-methylphenyl)phosphine (Strem Chemicals, Inc.), tris(*p*-fluorophenyl)phosphine (Strem Chemicals, Inc.), tris(*p*-trifluoromethylphenyl)phosphine (Strem Chemicals, Inc.), and methylene chloride (HPLC-MS) (Fisher Scientific). *p*-Methoxybenzyl alcohol, *p*-methylbenzyl alcohol, *p*-bromobenzyl alcohol, *p*-fluorobenzyl alcohol, and *p*-(trifluoromethyl)benzyl alcohol were purchased from Lancaster Synthesis. Benzyl alcohol was fractionally distilled from CaH₂, while benzaldehyde was fractionally distilled from MgSO₄. Benzyl- α,α -d₂ alcohol was prepared by the reduction of the ethyl benzoate with LiAlD₄ by a previously reported procedure.¹¹ All aqueous reactions used house-distilled water, which was passed through a Barnstead combination cartridge and an organic removal cartridge prior to use.

The ligand (P(C₆H₅)(*p*-C₆H₄CF₃)₂) was prepared by modifications of published procedures utilized for the synthesis of similar bisubstituted triphenylphosphine ligands.²⁷ The complexes [Ru(bpy)₂(Cl)(P(*p*-C₆H₄X)₃)](ClO₄)₂ were prepared by previously reported procedures.^{16,28} The complexes [Ru(H₂O)(bpy)₂(P(*p*-C₆H₄X)₃)](ClO₄)₂ (where X = OCH₃, CH₃, H, F, CF₃) were prepared by previously reported procedures,^{16,29} and the complex [Ru(H₂O)(bpy)₂(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ was prepared in an analogous manner. The complexes [Ru(bpy)₂(O)(P(*p*-C₆H₄X)₃)](ClO₄)₂ were prepared by synthetic modifications of the published procedure for the synthesis of [Ru(bpy)₂(O)(P(C₆H₅)₃)](ClO₄)₂,¹⁶ as described below.

Caution! While we have used perchlorate as a counterion with a number of ruthenium complexes without incident, perchlorate salts of metal complexes with organic ligands are potentially explosive. Care should be exercised in using a spatula or stirring rod to mechanically agitate any solid perchlorate. These complexes, as well as any other perchlorate salt, should be handled only in small quantities.^{30,31}

[Ru(H₂O)(bpy)₂(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ (**1**). To a 0.075-g sample of [Ru(bpy)₂(Cl)(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ (0.079 mmol) in 130 mL of H₂O was added dropwise a solution of 0.025 g of AgClO₄ (0.120 mmol) in 20 mL of H₂O. The resulting orange suspension was then heated at 85 °C under N₂(g) for 10 h, then stored in a refrigerator for 8 h. The cooled solution was gravity filtered, and then excess NaClO₄ was added. The orange precipitate was then collected by vacuum filtration and washed with 5 mL of cold H₂O; yield (0.060 g) 75%. Anal. Calcd for C₄₀H₃₁N₄O₉PCl₂F₆Ru(2H₂O): C, 45.12; H, 3.31. Found: C, 45.33; H, 3.28. UV-vis max (H₂O, pH 2.00): 290 nm (ϵ 3.8 × 10⁴); 423 nm (ϵ 7.0 × 10³). UV-vis max (CH₂Cl₂): 290 nm (ϵ 3.6 × 10⁴); 425 nm (ϵ 7.2 × 10³).

[Ru(bpy)₂(O)(P(*p*-C₆H₄CH₃)₃)](ClO₄)₂ (**2**). In the absence of light, a solution of 0.60 mL of Ce(IV) (0.5 N H₂Ce(ClO₄)₆ in 6 N HClO₄) (0.130 mmol) and 25 mL of H₂O was added dropwise over a period of 10 min to 0.020 g of [Ru(H₂O)(bpy)₂(P(*p*-C₆H₄CH₃)₃)](ClO₄)₂ (0.021 mmol) in 75 mL of H₂O. The yellow suspension was stirred for an additional 2 min, followed by the addition of 2 mL of 0.33 M NaClO₄. The yellow-green precipitate was collected by vacuum filtration and washed with 5 mL of cold H₂O; yield (0.012 g) 60%. Anal. Calcd for C₄₁H₃₇N₄O₉PCl₂Ru(3H₂O): C, 49.90; H, 4.39. Found: C, 49.64; H, 4.14. UV-vis max (H₂O, pH 2.00): 298 nm (ϵ 2.2 × 10⁴).

The remaining oxo complexes, [Ru(bpy)₂(O)(P(*p*-C₆H₄X)₃)](ClO₄)₂ (where X = OCH₃, F, CF₃) were prepared as for **2**, and all of the complexes gave satisfactory analyses.

Measurements. Elemental analyses were conducted by Atlantic Microlabs, Norcross, GA. Electronic absorption spectra were carried out in methylene chloride and in pH = 2.00 NaNO₃/HNO₃ aqueous buffer (μ = 0.06 M) and measured with a Milton Roy Spectronic 3000 array spectrophotometer equipped with a Hewlett-Packard 7470A plotter. Cyclic

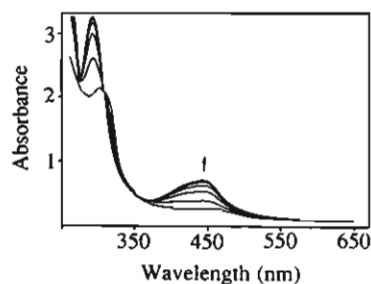


Figure 1. Spectral changes observed in the reaction of benzyl alcohol (2.7×10^{-3} M) with [Ru(bpy)₂(O)(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ (4.7×10^{-5} M) in methylene chloride at 25 °C.

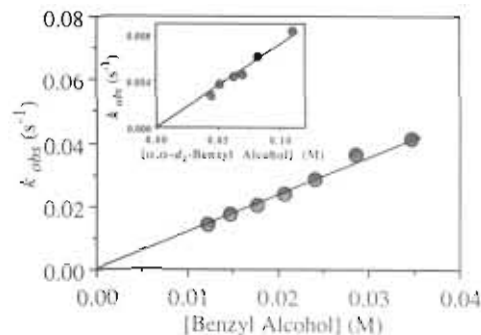


Figure 2. Plot of the observed pseudo-first-order rate constants (k_{obs}) as a function of benzyl alcohol concentrations for the oxidation of benzyl alcohol by [Ru(bpy)₂(O)(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ in methylene chloride at 25 °C. Inset: Corresponding plot for the oxidation of benzyl- α,α -d₂ alcohol by [Ru(bpy)₂(O)(P(C₆H₅)(*p*-C₆H₄CF₃)₂)](ClO₄)₂ in methylene chloride at 25 °C.

voltammetric and differential-pulse voltammetric experiments were carried out in pH = 2.00 K₂SO₄/H₂SO₄ aqueous buffer (μ = 0.20 M). A glassy-carbon working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel reference electrode (SSCE) were used for all electrochemical experiments. Prior to use the glassy-carbon working electrode was polished for 3 min utilizing a minimet polisher (Buehler Ltd.), 0.3 μ m alumina polishing compound (Buehler Ltd.), and 7.3 cm (diameter) polishing cloth (Buehler Ltd.), followed by sonication for 30 s in water. Voltammetric experiments were conducted with an IBM EC/225 polarographic analyzer equipped with a Houston Instruments Model 100 recorder. All separations were performed using a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector and either a 0.32 mm i.d., 5% diphenyl polysiloxane column, or a 0.53 mm i.d., 100% dimethyl polysiloxane column (Restek Corporation). Kinetic studies were carried out spectrophotometrically using Beckman DU spectrophotometers that were retrofitted with Gilford accessories. The cell blocks in the spectrophotometers were maintained at 25 °C by the use of thermostatted water baths.

Kinetic Procedure. The kinetics of the oxidation of benzyl alcohol and the para-substituted benzyl alcohols were conducted in methylene chloride and in pH = 2.00 NaNO₃/HNO₃ aqueous buffer (μ = 0.06 M) at 25 °C and monitored spectrophotometrically at the wavelength maximum corresponding to the formation of [Ru(H₂O)(bpy)₂(P(*p*-C₆H₄X)₃)](ClO₄)₂. Pseudo-first-order conditions were maintained, where a minimum of a 50-fold excess of benzyl alcohol was utilized. Kinetics plots were exponential and yielded pseudo-first-order rate constants proportional to substrate concentration. The accuracies of the measurements for all of the second-order-rate constants were within 10% at a 95% confidence limit.

Product Analysis. The oxidation of benzyl alcohol and the para-substituted benzyl alcohols was conducted under an atmosphere of dinitrogen at 25 °C and the benzaldehyde or the para-substituted benzaldehyde formed was analyzed by gas chromatography. The ruthenium products were characterized by electronic spectroscopy. The oxidation of the benzyl alcohols by [Ru(bpy)₂(O)(P(*p*-C₆H₄X)₃)](ClO₄)₂ complexes conducted in methylene chloride and in pH = 2.00 NaNO₃/HNO₃ aqueous buffer (μ = 0.06 M) produced only the benzaldehyde in 80–95% yield, plus the analogous [Ru(H₂O)(bpy)₂(P(*p*-C₆H₄X)₃)](ClO₄)₂ complexes in quantitative yields.

(27) Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* **1960**, *25*, 2001.

(28) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(29) Leising, R. A.; Ohman, J. S.; Takeuchi, K. *J. Inorg. Chem.* **1988**, *27*, 3804.

(30) Wosley, W. C. *J. Chem. Educ.* **1973**, *50*, A335.

(31) Raymond, K. *Chem. Eng. News* **1983**, *61* (Dec. 5), 4.

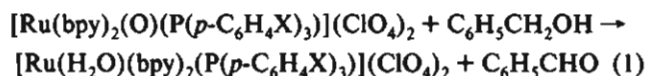
Table I. $E_{1/2}$ Potentials for the Ruthenium(IV)/Ruthenium(III) Couples of $[\text{Ru}(\text{bpy})_2(\text{O})(\text{Y})](\text{ClO}_4)_2$ Complexes and Second-Order Rate Constants at 25 °C for the Oxidation of Benzyl Alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{Y})](\text{ClO}_4)_2$

Y	$E_{1/2}$ (V vs SSCE) ^a	solvent	k ($\text{M}^{-1} \text{s}^{-1}$) ^b
$\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	1.02	CH_2Cl_2	0.28 ± 0.03
		H_2O^c	0.47 ± 0.02
$\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$	1.03	CH_2Cl_2	0.34 ± 0.03
		H_2O^c	0.49 ± 0.03
$\text{P}(\text{C}_6\text{H}_5)_3$	1.05	CH_2Cl_2	0.45 ± 0.04
		H_2O^c	0.58 ± 0.05
$\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$	1.08	CH_2Cl_2	0.68 ± 0.04
		H_2O^c	0.85 ± 0.04
$\text{P}(\text{C}_6\text{H}_5)(p\text{-C}_6\text{H}_4\text{CF}_3)_2$	1.12	CH_2Cl_2	1.18 ± 0.09
		H_2O^c	1.80 ± 0.05
$\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$	1.17	CH_2Cl_2	1.66 ± 0.14
		H_2O^c	2.36 ± 0.31

^a Conditions: differential pulse voltammetry; pH = 2.00 in $\text{K}_2\text{SO}_4/\text{H}_2\text{SO}_4$ aqueous buffer ($\mu = 0.06$); glassy-carbon working electrode; saturated sodium chloride reference electrode SSCE; scan rate = 5 mV/s. ^b Uncertainty at 95% confidence limits. ^c Solvent: pH = 2.00 in $\text{NaNO}_3/\text{HNO}_3$ aqueous buffer ($\mu = 0.06 \text{ M}$).

Results

Spectral and Kinetic Studies. The oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes, (where X = OCH_3 , CH_3 , H, F, CF_3) in methylene chloride and aqueous solution proceeds as illustrated in eq 1. Spectrophotometric



changes display isosbestic behavior for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes, where $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ was cleanly converted to $[\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$, (see Figure 1). The kinetics for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes were determined to be second-order overall, first-order in both substrate and oxidant. The linear plot of k_{obs} vs benzyl alcohol concentration clearly demonstrates the first-order dependency on benzyl alcohol (Figure 2). The results of the kinetic studies conducted in both aqueous solution and methylene chloride are given in Table I.

Deuterium Labeling Studies. Kinetic isotope effects for the oxidation of benzyl- $\alpha,\alpha\text{-d}_2$ alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)](\text{ClO}_4)_2$ and $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)(p\text{-C}_6\text{H}_4\text{CF}_3)_2)](\text{ClO}_4)_2$ were determined in methylene chloride at 25 °C and display large deuterium isotope effects ($k_{\text{H}}/k_{\text{D}}$) of 17 ± 2 and 13 ± 2 respectively. These isotopic ratios are considerably larger than the maximum value of 6.9 that is attributable to the zero-point-energy differences between C–H and C–D bonds.^{32,33} Large isotopic ratios have been observed for other reactions involving a transfer of a proton, hydrogen atom, or a hydride ion and are believed to be at least in part due to quantum-mechanical tunneling.³⁴

Phosphine Electronic Effects. The use of para-substituted triphenylphosphine ligands allows for the control of electronic properties of the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes, while constant steric properties are maintained.¹⁷ A plot of the $E_{1/2}$ values of the ruthenium(IV)/ruthenium(III) couples (Table I), as a function of $\sum\sigma_p$ (σ_p = Hammett substituent constant for para-substituents)³⁵ yields a linear relationship, with $\rho = +0.06 \pm 0.01$. This linear relationship indicates that the electronic effects

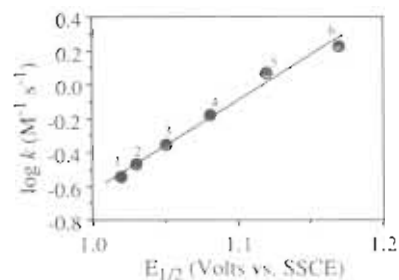


Figure 3. Plot of the log of the second-order rate constants (k) for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes as a function of the observed $E_{1/2}$ values for the ruthenium(IV)/ruthenium(III) redox couple for these complexes. The phosphine ligands used were (1) $\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3$, (2) $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$, (3) $\text{P}(\text{C}_6\text{H}_5)_3$, (4) $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$, (5) $\text{P}(\text{C}_6\text{H}_5)(p\text{-C}_6\text{H}_4\text{CF}_3)_2$, and (6) $\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$. The oxidation reactions were conducted in methylene chloride at 25 °C.

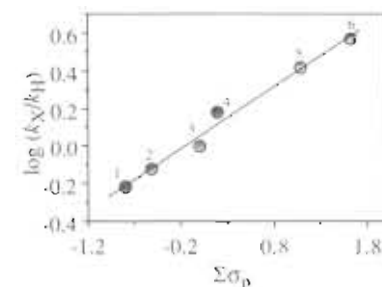


Figure 4. Plot of $\log(k_{\text{X}}/k_{\text{H}})$ as a function of the summation of the Hammett substituent constants (σ_p) for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes at pH = 2.00 ($\text{NaNO}_3/\text{HNO}_3$ aqueous buffer; $\mu = 0.06 \text{ M}$) at 25 °C. The phosphine ligands used were (1) $\text{P}(p\text{-C}_6\text{H}_4\text{OCH}_3)_3$, (2) $\text{P}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$, (3) $\text{P}(\text{C}_6\text{H}_5)_3$, (4) $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$, (5) $\text{P}(\text{C}_6\text{H}_5)(p\text{-C}_6\text{H}_4\text{CF}_3)_2$, and (6) $\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$.

associated with the para-substituted triphenylphosphine ligands are transmitted to the ruthenium center.^{26,29}

The potentials of the ruthenium(IV)/(III) redox couples of the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes have a direct effect on the values of the second-order rate constants for the oxidation of benzyl alcohol. A plot of $\log k$ vs $E_{1/2}$ for the oxidation reactions conducted in methylene chloride yields a linear relationship with a slope of $+5.2 \pm 1.0$ (Figure 3). The relationship between $\log k$ and $E_{1/2}$ is given by eq 2. Similarly, a plot of \log

$$\log k = (5.2 \pm 1.0)E_{1/2} - 5.9 \pm 1.1 \quad (2)$$

k vs $E_{1/2}$ for the reactions conducted in aqueous solution also displays a linear relationship and is represented by eq 3. The

$$\log k = (5.1 \pm 1.2)E_{1/2} - 5.6 \pm 1.3 \quad (3)$$

relationship $\log k = (\alpha)16.9E_{1/2} + C$ at 25 °C has been shown to be equivalent to the Brønsted relationship $\log k = (\alpha) \log K + C$, where the Brønsted parameter α can be obtained from $\log k$ versus $E_{1/2}$ plots.^{20,36,37} The slopes obtained from the plots of $\log k$ vs $E_{1/2}$ correspond to α values of 0.31 ± 0.06 (methylene chloride) and 0.30 ± 0.07 (water).

The electronic ligand effects of the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes on the second-order rate constants for the oxidation of benzyl alcohol can also be expressed in terms of Hammett parameters ($\sum\sigma_p$), where plots of $\log(k_{\text{X}}/k_{\text{H}})$ vs $\sum\sigma_p$ for the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes yield linear relationships with $\rho = +0.33 \pm 0.06$ (methylene chloride) and $\rho = +0.31 \pm 0.09$ (water) (see Figure 4). Also, the use of Kabachnik's σ_{ph} substituent constants,³⁸ which have been utilized

(32) Bell, R. P. *Chem. Soc. Rev.* 1974, 3, 513.

(33) Scott, A. F., Ed. *Survey of Progress in Chemistry*; John Wiley & Sons: New York, 1966; p 109.

(34) Isaacs, N. S. *Physical Organic Chemistry*; John Wiley & Sons: New York, 1987; p 269.

(35) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* 1958, 23, 420.

(36) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* 1980, 102, 2928.

(37) Ng, F. T. T.; Henry, P. M. *J. Am. Chem. Soc.* 1976, 98, 3606.

Table II. $E_{1/2}$ Potentials for the One-Electron Oxidation of Alcohols, and Second-Order Rate Constants for the Oxidation of Benzyl Alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$ at 25 °C

substrate	$E_{1/2}$ (V vs Ag/AgCl) ^a	solvent	10^2k ($\text{M}^{-1} \text{s}^{-1}$) ^{b,c}
methanol	3.57	CH_3CN	0.058 ± 0.002
		H_2O^d	0.025 ± 0.001
ethanol	3.26	CH_3CN	0.16 ± 0.001
		H_2O^d	0.052 ± 0.002
1-propanol	3.05	CH_3CN	0.30 ± 0.02
		H_2O^d	0.079 ± 0.002
2-propanol	2.97	CH_3CN	0.72 ± 0.05
		H_2O^d	0.23 ± 0.01
1-butanol	2.92	CH_3CN	0.27 ± 0.02
		H_2O^d	0.11 ± 0.002
1-pentanol	2.87	CH_3CN	0.30 ± 0.02
		H_2O^d	0.15 ± 0.008
benzyl alcohol	1.63	CH_3CN	83 ± 13
		H_2O^d	105 ± 5.0

^a Extrapolated from gas-phase ionization potentials to acetonitrile versus Ag/AgCl as described in ref 40 and in the text. ^b Second-order rate constants from ref 14. ^c Uncertainty at 95% confidence limits. ^d Solvent: pH = 2.00 in $\text{NaNO}_3/\text{HNO}_3$ aqueous buffer ($\mu = 0.06 \text{ M}$).

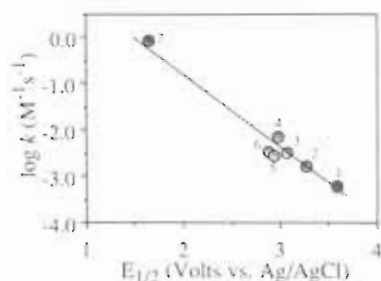


Figure 5. Plot of the log of the second-order rate constant (k) for the oxidation of alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$ as a function of the calculated $E_{1/2}$ values for the one-electron oxidation of alcohols. The alcohols used were (1) methanol, (2) ethanol, (3) 1-propanol, (4) 2-propanol, (5) 1-butanol, (6) 1-pentanol, and (7) benzyl alcohol. The oxidation reactions were conducted in acetonitrile at 25 °C, and the second-order rate constants were obtained from ref 14.

to correlate the electronic effects associated with tertiary phosphine ligands, also yields straight lines, with $\rho = +0.40 \pm 0.17$ (methylene chloride) and $\rho = +0.27 \pm 0.13$ (water).

In addition to linear free energy correlations between the log k for the oxidation of benzyl alcohol and the electronic ligand effects of the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes, we can utilize previously reported kinetic data (see Table II) to construct a linear free energy correlation for the oxidation of various primary and secondary alcohols by a single oxoruthenium complex, $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$. The $E_{1/2}$ values associated with the one-electron oxidation of primary and secondary alcohols (see Table II) were derived from the gas-phase ionization potentials³⁹ in a manner analogous to the determination of the one-electron potentials associated with alkenes,²⁰ utilizing the relationship $E_{1/2} = 0.827I_p - 5.40 \text{ V}$.⁴⁰ For the oxidation reactions conducted in acetonitrile a plot of log k vs $E_{1/2}$ for the oxidation of primary and secondary alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$ yields a straight line (see Figure 5 and eq 4). Similarly, a plot of log k vs $E_{1/2}$ for the

$$\log k = (-1.6 \pm 0.4)E_{1/2} + 2.5 \pm 1.0 \quad (4)$$

reactions conducted in aqueous solution also displays a linear relationship (see eq 5). The slopes of -1.6 ± 0.4 (acetonitrile)

$$\log k = (-1.9 \pm 0.4)E_{1/2} + 3.0 \pm 1.0 \quad (5)$$

and -1.9 ± 0.4 (water) can be converted to the Brønsted α values of 0.09 ± 0.02 (acetonitrile) and 0.11 ± 0.02 (water) for the oxidation of alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PPh}_3)](\text{ClO}_4)_2$.

Substrate Electronic Effects. The rate constants of the oxidation of para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PPh}_3)](\text{ClO}_4)_2$ were measured (see Table III). Plots of the log(k_X/k_H) data versus the Hammett substituent constants, σ , σ^+ , or σ^- gave scattered plots with low R^2 values. However, the kinetic data were then further analyzed by using the modified Hammett equation, (6). In eq 6, σ^* is the free radical substituent

$$\log(k_X/k_H) - \sigma^* = \rho\sigma \quad (6)$$

constant developed by Fisher.⁴¹ The plot of log(k_X/k_H) - σ^* versus σ gave an excellent correlation for the oxidation of the para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PPh}_3)](\text{ClO}_4)_2$ in methylene chloride with $\rho = -0.57 \pm 0.07$, $R^2 = 0.99$ (see Figure 6). For the rate constant data for the oxidation of the para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PPh}_3)](\text{ClO}_4)_2$ in water, the plot of log(k_X/k_H) - σ^* versus σ^* gave a poor correlation, with $\rho = -0.34 \pm 0.36$, $R^2 = 0.80$.

Solvent Effect. The oxidation of benzyl alcohol by the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes in methylene chloride and in water showed no solvent effect as can be seen from the ρ values, $\rho = +0.33 \pm 0.06$ (in CH_2Cl_2) and $\rho = +0.31 \pm 0.09$ (in H_2O). By contrast, the oxidation of the para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PPh}_3)](\text{ClO}_4)_2$ showed that the second-order rate constants for the oxidation in water are approximately twice the values obtained in methylene chloride with the exception of the unsubstituted benzyl alcohol which has the same value in both solvents.

Discussion

Phosphine Electronic Effects. The results of the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes clearly demonstrate that the rate of oxidation is dependent on the electronic properties of the oxoruthenium complexes. The value of ρ , obtained from the Hammett equation, has been utilized as a measure of the charge distribution in the transition state, and has been also shown to be sensitive to subtle changes in the mechanism of chemical processes.⁴²⁻⁴⁴ The relatively small positive ρ values of approximately +0.3 obtained in our oxidation reactions are reminiscent of the small positive ρ values for reactions in which there is only a small increase of negative charge in the transition state.⁴⁵

For reactions in which the one-electron redox potentials can be obtained, the determination of the degree of electron transfer or the fraction of charge associated with an oxidation reaction can be readily obtained from the linear free energy relationship between the log of the second-order rate constants and the $E_{1/2}$ values.^{20,36} The Brønsted parameter (α), which can be obtained from the slope of the plot of log k vs $E_{1/2}$ values, has been shown to be approximately equal to the fractional displacement of the transition state along the reaction coordinate from reactants to products.^{43,46} The small α values of 0.09 ± 0.02 (acetonitrile) and 0.11 ± 0.02 (water) obtained for the oxidation of a variety of alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$, in conjunction with small α values of 0.31 ± 0.06 (methylene chloride) and

(38) Mastryukova, T. A.; Kabachnik, M. I. *Russ. Chem. Rev. (Engl. Transl.)* 1969, 38, 795.

(39) Lias, S. G.; Bartmess, J. E.; Liebman, I. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, 17, Suppl. No. 1.

(40) Niekman, W. C.; Dimeler, G. R.; Desmond, M. M. *J. Electrochem. Soc.* 1964, 111, 1190.

(41) Fisher, T. H.; Meierhoefer, A. W. *J. Org. Chem.* 1978, 43, 224.

(42) Hammett, L. P. *Physical Organic Chemistry Reaction Rates, Equilibria, and Mechanism*; McGraw-Hill: New York, 1970; p 347.

(43) Wells, R. P. *Linear Free Energy Relationships*; Academic Press: New York, 1970.

(44) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; John Wiley & Sons: New York, 1963; p 128.

(45) Bunting, J. W.; Sindhuatmadja, S. *J. Org. Chem.* 1981, 46, 4211.

(46) Leffler, J. E. *Science* 1953, 117, 340.

Table III. Second-Order Rate Constants for the Oxidation of Para-Substituted Benzyl Alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)(\text{ClO}_4)_2]$ in Methylene Chloride and in Water at 25 °C

para substituent	solvent	k ($\text{M}^{-1} \text{s}^{-1}$) ^a	para substituent	solvent	k ($\text{M}^{-1} \text{s}^{-1}$) ^a
OCH ₃	CH ₂ Cl ₂	0.54 ± 0.08	F	CH ₂ Cl ₂	0.29 ± 0.02
	H ₂ O ^b	1.29 ± 0.09		H ₂ O ^b	0.48 ± 0.04
CH ₃	CH ₂ Cl ₂	0.61 ± 0.05	Br	CH ₂ Cl ₂	0.55 ± 0.08
	H ₂ O ^b	0.97 ± 0.09		H ₂ O ^b	1.12 ± 0.10
H	CH ₂ Cl ₂	0.45 ± 0.04	CF ₃	CH ₂ Cl ₂	0.53 ± 0.05
	H ₂ O ^b	0.58 ± 0.04		H ₂ O ^b	1.02 ± 0.10

^a Uncertainty at 95% confidence limits. ^b Solvent: pH = 2.00 in NaNO₃/HNO₃ aqueous buffer ($\mu = 0.06 \text{ M}$).

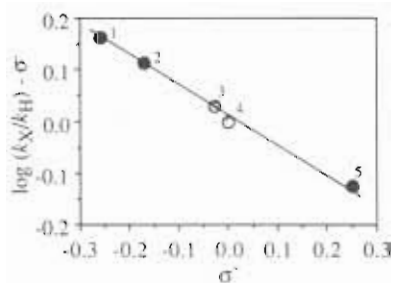


Figure 6. Plot of $\log(k_X/k_H) - \sigma^*$ versus σ^* for the oxidation of para-substituted benzyl alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)(\text{ClO}_4)_2]$ in methylene chloride at 25 °C. The data for *p*-CF₃ has been omitted because of the unavailability of the σ^* value for CF₃. The *p*-XC₆H₄CH₂OH compounds used were (1) X = OCH₃, (2) X = CH₃, (3) X = F, (4) X = H, and (5) X = Br.

0.30 ± 0.07 (water) obtained for the oxidation benzyl alcohol by a variety of $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_4\text{X})_3)(\text{ClO}_4)_2]$ complexes are similar to α values for reactions such as the oxidation of alkenes by oxochromium(V) porphyrin complexes, where $\alpha = 0.18$ when the alkene is varied and $\alpha = 0.55$ when the porphyrin is varied.²⁰ The existence of small α values has been suggested to indicate that only partial charge transfer in the rate-determining step has occurred.²⁰

A more quantitative interpretation of the progress along the reaction coordinate can be obtained from the α values for substrate oxidation as presented by Bruice,²⁰ where α is a combination of the Leffler–Hammond contribution (χ) and the Thornton contribution ($0.5(\tau - 1)$) and is represented by eq 7. The Leffler–

$$\alpha = \chi \pm 0.5(\tau - 1) \quad (7)$$

Hammond contribution is a measure of the progress of the reaction along the reaction coordinate, while the Thornton contribution is a measure of the “tightness” of the transition state.^{20,46–49} The values associated with χ and τ can be readily determined from eq 7, utilizing the α values obtained from the reaction of primary and secondary alcohols with $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)(\text{ClO}_4)_2]$ and the reaction of benzyl alcohol with $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_4\text{X})_3)(\text{ClO}_4)_2]$. For the reactions conducted in nonaqueous solutions (acetonitrile or methylene chloride) $\chi = 0.21$ and $\tau = 0.77$, while in aqueous solution $\chi = 0.21$ and $\tau = 0.81$. The reaction of alcohols with $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_4\text{X})_3)(\text{ClO}_4)_2]$ complexes can be best described by a reaction in which the transition state associated with charge transfer is located $\approx 20\%$ along the reaction coordinate and is moderately “loose”. Accordingly, the transition state might be envisaged as involving more C–H bond breaking relative to Ru=O–H bond formation.

Substrate Electronic Effect. The effect of para-substituents on the oxidation of benzyl alcohol in methylene chloride and in water by $[\text{Ru}(\text{bpy})_2(\text{O})\text{PPh}_3](\text{ClO}_4)_2$ showed no linear correlation of $\log(k_X/k_H)$ versus any of the substituent constants σ , σ^+ , or

σ^- . This observation illustrates that the oxidation of para-substituted benzyl alcohols does not involve a pure resonance stabilizing situation, where electron-donating groups accelerate and electron-withdrawing groups decelerate a reaction involving an electron deficient transition state.⁵⁰ Substituent effects similar to our nonlinear correlation have been reported for the dissociation of hexaarylethanes,⁵¹ the reactivity of aromatic compounds in the reaction with phenyl radicals,^{52,53} the thermal decomposition of substituted dibenzyl mercury compounds,⁵⁴ and the abstraction of the benzylic hydrogen atom from substituted dibenzyl ethers by benzoyloxy and *tert*-butoxy radicals.^{55,56} The similarity of our results with reactions which involve radical character in the transition state prompted us to examine our results from the point of view of a radical mechanism.

Various models have been made to develop substituent constants for studying substituent effects in radical mechanisms.^{41,57–63} The Fisher model is based on the reaction of *N*-bromosuccinimide with para-substituted 3-cyanotoluenes in which Br atom abstracts a hydrogen from the benzylic carbon in the rate-determining step.⁴¹ We applied the free radical substituent constant σ^* developed by Fisher to treat our kinetic data obtained in methylene chloride, and we found that σ^- values best fit with the corresponding $\log(k_X/k_H) - \sigma^*$ values, where σ^- is the radical substituent constant. An excellent correlation was obtained in the plot of $\log(k_X/k_H) - \sigma^-$ versus σ^- with $\rho = -0.57 \pm 0.07$ and $R^2 = 0.99$. We also applied the Fisher analysis to our kinetic data obtained in water, and we found that σ^+ values best fit with the corresponding $\log(k_X/k_H) - \sigma^+$ values. However the correlation of $\log(k_X/k_H) - \sigma^+$ versus σ^+ for our data obtained in water yielded a poor correlation, with $\rho = -0.34 \pm 0.36$ and $R^2 = 0.80$. Although the correlation is poor, the use of σ^+ with the data taken in water can probably be interpreted as evidence of a polar transition state with benzylic cation character. Intuitively, this type of transition state is anticipated in the oxidation of benzyl alcohol. Thus, the correlation of $\log(k_X/k_H) - \sigma^-$ versus σ^- for the data obtained in methylene chloride is surprising. Although radical reactions have commonly been found to give good correlations of $\log(k_X/k_H)$ versus σ or σ^+ , Zavitsas⁶⁴ has shown that a number of reactions which give excellent correlations with σ or σ^+ actually give the best correlations with σ^- . Also Jaffé's review mentions that σ^- constants better represent some free radical reactions.⁶⁵ One possible interpretation of the σ^+ and the σ^- correlations is that solvent water should stabilize a charged transition state, and thus a cationic transition state is observed with water as the solvent. With methylene chloride as the solvent, a charged transition state might be suppressed. As a result, σ^- correlations in methylene chloride could then be due to hyperconjugation effects in the ground state of the target para-substituted benzyl alcohols.

Our kinetic data is reminiscent of the data obtained by Roecker and Meyer¹¹ for the oxidation of benzyl alcohol with $[\text{Ru}(\text{bpy})_2(\text{O})(\text{py})]^{2+}$ in acetone/water and acetonitrile. However, the authors did not apply the Fisher analysis to their results. We

(47) Kreevoy, M. M.; Lee, I. S. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550.
 (48) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
 (49) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

(50) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *105*, 1221.
 (51) Roy, M. F.; Marvel, C. S. *J. Am. Chem. Soc.* **1937**, *59*, 2622.
 (52) Augood, D. R.; Hey, D. H.; Williams, G. H. *J. Chem. Soc.* **1952**, 2094.
 (53) Dannely, R. L.; Gregg, Jr. E. C.; Phelps, R. E.; Coleman, C. B. *J. Am. Chem. Soc.* **1954**, *76*, 445.
 (54) Dincturk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., Chem. Commun.* **1979**, 172.
 (55) Huang, R. L.; Singh, S. *J. Chem. Soc.* **1959**, 3183.
 (56) Huang, R. L.; Yeo, Oon-Keong. *J. Chem. Soc.* **1959**, 3190.
 (57) Dinckurt, S.; Jackson, R. A.; Townson, M.; Agirbas, H.; Billingham, N. C.; March, G. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1121.
 (58) Yamamoto, T.; Otsu, T. *Chem. Ind. (London)* **1967**, 787.
 (59) Sakurai, H.; Hayashi, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945.
 (60) Alfrey, T.; Price, C. C. *J. Polym. Sci.* **1947**, *2*, 101.
 (61) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221.
 (62) Creary, X. *J. Org. Chem.* **1980**, *45*, 280.
 (63) Ito, R.; Migita, T.; Morikawa, N.; Simamura, O. *Tetrahedron* **1965**, *21*, 955.
 (64) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.
 (65) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191.

therefore applied the Fisher analysis to the data obtained by Roecker and Meyer, and we observed that σ^+ gave the best correlation with $\log(k_X/k_H) - \sigma^+$ for acetone/water, $\rho = -0.25 \pm 0.17$ ($R^2 = 0.88$), and also for acetonitrile, $\rho = -0.35 \pm 0.28$ ($R^2 = 0.83$). Because these correlations are not good ($R^2 < 0.9$), there can be no conclusive statements made about the nature of the transition state. However, the signs and magnitudes of the calculated ρ values are at least consistent with benzyl alcohol oxidation, and thus these Fisher analyses appear to yield more insight than the plots of $\log k$ versus σ reported by Roecker and Meyer. Notably, we observed that σ^+ gave the best correlations for both reactions. This observation is in agreement with our earlier conclusion that the more polar solvents (water, acetone/water and acetonitrile) stabilize a charged transition state whereas methylene chloride suppresses the charged transition state.

Deuterium Labeling Studies. The oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)](\text{ClO}_4)_2$ or $[\text{Ru}(\text{bpy})_2(\text{O})(\text{C}_6\text{H}_5\text{-P}(p\text{-C}_6\text{H}_4\text{CF}_3)_2)](\text{ClO}_4)_2$ proceeds with $\alpha\text{-C-H}$ isotope effects (k_H/k_D) of 17 ± 2 and 13 ± 2 , respectively. These large primary isotope effects are reminiscent of the value of 10 obtained for the oxidation of 2-propanol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{C}_6\text{H}_5)_3)](\text{ClO}_4)_2$,¹⁴ a value of 16 obtained for the oxidation of α -(trifluoromethyl)-benzyl alcohol by MnO_4^- ,⁶⁶ and values of 9 and 24 obtained for the oxidation methanol and benzhydrol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{py})]^{2+}$ respectively.¹¹ The (k_H/k_D) values obtained in this work are much smaller than the values reported by Roecker and Meyer¹¹ where (k_H/k_D) = 50 was obtained for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{py})]^{2+}$. Recently, Che and co-workers⁶⁷ reported (k_H/k_D) values in the range 15–19 for the oxidation of benzyl alcohol by a series of *trans*-dioxoruthenium(VI) complexes. Quantum mechanical tunneling has been invoked in order to explain large (>6.9) deuterium isotopic ratios.³⁴ Quantum mechanical tunneling has been suggested for proton, hydrogen atom, and hydride transfer reactions, therefore large (k_H/k_D) ratios are not indicative of any particular atom transfer pathway.³² Deuterium isotopic ratios of 8–100 have been observed where the magnitude is believed to be dependent on the degree of steric hindrance, the magnitude of the activation, and the degree of solvation associated with the atom being transferred.³⁴ Although the presence of large (k_H/k_D) ratios for the oxidation of alcohols by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes does suggest

that $\alpha\text{-C-H}$ bond breaking does occur in the rate-determining step, the degree of bond breaking cannot be interpreted in terms of the magnitude of the (k_H/k_D) ratios alone.

Solvent Effects. For our experiments the linear free energy relationships for the oxidation of benzyl alcohol when the phosphine ligand of the oxidant is varied demonstrate that there is no solvent effect associated with the magnitude of the ρ values. The Hammett linear free energy relationship between $\log(k_X/k_H)$ and the $\Sigma\sigma_p$ for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ yielded $\rho = 0.33 \pm 0.06$ for reactions conducted in methylene chloride and $\rho = 0.31 \pm 0.09$ for reactions conducted in aqueous solution. Since it has been demonstrated that the magnitude of ρ is generally dependent on the dielectric constant of the solvent,⁴² the active site associated with the transition state for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ must be shielded from the solvent. More specifically, since the para-substituents of the tertiary phosphine ligands affect only the energy of the $\text{Ru}=\text{O}$ bond, the solvent effect indicates that the $\text{Ru}=\text{O}$ bond is effectively shielded from the solvent. This observation corroborates the mechanism proposed earlier for the hydrophobic effect involved in the oxidation of aliphatic alcohols in aqueous media by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(\text{R})_3)](\text{ClO}_4)_2$, where it was suggested that the tertiary phosphine ligand inhibits water solvation of the oxo ligand.¹⁴

Conclusions. The unique aspect of this report lies in our study of the substituent electronic effects for *both* the ruthenium-based oxidants and the target alcohol substrates. All of our studies combine to yield a consistent image of the mechanism for the oxidation of benzyl alcohol by $[\text{Ru}(\text{bpy})_2(\text{O})(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)](\text{ClO}_4)_2$ complexes, where we propose that in the rate-determining step a partial hydrogen atom abstraction from the target benzyl alcohol occurs in the transition state, yielding intermediates consisting of a hydroxyruthenium(III) complex and a benzyl alcohol radical. This rate-determining step is followed by a rapid reaction of the hydroxyruthenium(III) complex and the benzyl alcohol radical to form an aquaruthenium(II) complex and benzaldehyde.

Acknowledgment. This work was supported in part by the donors of the National Science Foundation (CHE 9120602) and the ARCO Chemical Co. We are grateful to Johnson Matthey for the generous loan of ruthenium trichloride trihydrate.

(66) Stewart, R.; van der Linden, R. *Discuss. Faraday Soc.* 1960, 29, 211.

(67) Che, C. M.; Tang, W. T.; Lee, W. O.; Wong, K. Y.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* 1992, 1551.