

## International Journal of Scientific Research and Reviews

### Reduction mechanism of a coordinated superoxide by benzyl alcohol and 2-propanol

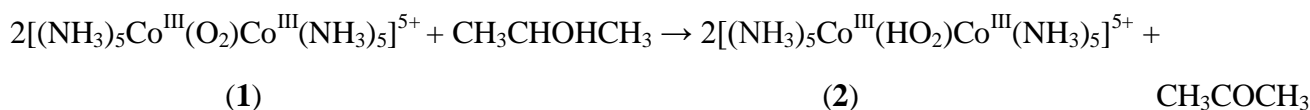
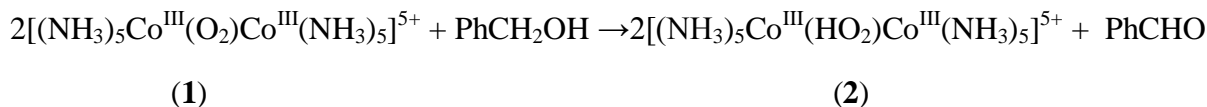
Ritu Mukherjee

Department of Chemistry, Dum Dum Motijheel College, Kolkata 700 074, West Bengal India.

E-mail: [ritu069@gmail.com](mailto:ritu069@gmail.com)

#### ABSTRACT

In aqueous acetate buffer media, Benzyl alcohol and 2-propanol reduces the bridging superoxide in  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$  (**1**) to corresponding peroxide in the complex,  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2\text{H})\text{Co}^{\text{III}}(\text{NH}_2)(\text{NH}_3)_4]^{4+}$  (**2**), the reductants being oxidized to benzaldehyde and acetone respectively. The complex **2** thus produced decomposes rapidly to the final products,  $\text{Co}^{\text{II}}$ ,  $\text{NH}_3$ , etc. instead of reacting with a second molecule of reductants. In the presence of excess reductants over **1**, the reaction obeyed first-order kinetics and exhibited inverse proton dependence.  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}((\text{NH}_2)(\text{NH}_3)_4)]^{4+}$  (**3**), a conjugate base of **1**, seems to be the kinetically reactive species and the cause for the observed inverse proton dependence. Reaction rate with the reductants significantly decreases with increasing proportion of  $\text{D}_2\text{O}$  replacing water in the solvent and the rate-limiting step seems to be an H-atom transfer.



**KEYWORDS:** Metal superoxide, Benzyl alcohol, 2-propanol, redox reaction kinetics, H-atom Transfer.

**\*Corresponding author:**

**Ritu Mukherjee**

Department of Chemistry,

Dum Dum Motijheel College,

Kolkata 700 074, West Bengal India.

E-mail: [ritu069@gmail.com](mailto:ritu069@gmail.com)

## INTRODUCTION

Free-radical-mediated per oxidation of membrane lipids<sup>1</sup> and oxidative damage of DNA are associated with a variety of chronic health problems, such as cancer, inflammation, atherosclerosis, neurodegenerative processes and aging.<sup>2</sup> The first step in the oxygen activation mechanisms of metalloenzymes is typically the binding of dioxygen, resulting in electron transfer from metal to O<sub>2</sub> to form a metal-superoxo species.<sup>3</sup> The superoxide radical anion, O<sub>2</sub><sup>-</sup> has thus been implicated as a byproduct of the functioning of aerobic organisms<sup>4</sup> Consequently, the reactions of superoxide are of special interest. Superoxide is a strong nucleophile, which can form reasonably robust metal complexes in the absence of facile decomposition paths.<sup>5</sup> Present work deals with the mechanism for base-catalyzed oxidation of benzyl alcohol and 2-propanol to benzaldehyde and 2-propanone respectively by bridging superoxide ligand in the dinuclear complex, [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>(O<sub>2</sub>)Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>5+</sup> (**1**), towards Benzyl alcohol and 2-propanol in the pH interval 4.7–5.45 maintained by acetate buffer.

## MATERIALS AND METHODS

### Materials

μ-superoxobis[pentaamminecobalt(III)] chloride, [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>(O<sub>2</sub>)Co<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>5</sub>, (**1**) was synthesised by the literature process.<sup>6</sup> The chloride salt was converted to the corresponding perchlorate salt<sup>7</sup> and recrystallized from 10% HClO<sub>4</sub>. [ε (M<sup>-1</sup> cm<sup>-1</sup>) at 670 nm: found 832, reported<sup>8</sup> 838]. Benzyl alcohol and 2-propanol (G.R, E. Merck) were used without further purification. Only fresh stocks of Benzyl alcohol and 2-propanol were used for kinetic and stoichiometric studies. Sodium perchlorate solution for maintenance of ionic strength in kinetic measurements was prepared from NaHCO<sub>3</sub> and HClO<sub>4</sub>. All other materials used were of reagent grade and used without further purification.

### Instrumentation

Absorbance and UV-VIS spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cell. The kinetics was monitored *in situ* in the electrically controlled thermostated (25.0 ± 0.1 °C) cell housing (CPS – 240 A) at 670 nm, the visible absorption maximum of **1**. The reactions were studied in acetate buffer (pH, 4.7–5.45; total acetate, T<sub>OAc</sub> = 0.20 M) using a large excess of peroxide over **1**. A pH meter (Toshniwal CL-54, India) with electrodes calibrated with standard buffer solutions was used for pH measurements. Media ionic strength for kinetic studies was adjusted to 0.50 M (NaClO<sub>4</sub>). All solutions were prepared in doubly distilled and then freshly boiled water. Reaction media were de-aerated with argon prior to kinetic measurements.

Observed first-order rate constants ( $k_o$ ) were extracted by non-linear least-squares fitting of the decay of the absorbance ( $A_t$ ) of **1** versus time (t) data to standard first-order exponential decay equation.

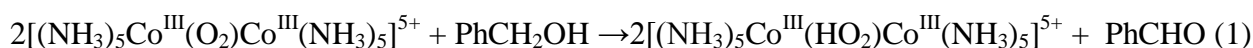
### Stoichiometry

The stoichiometry of the reaction was determined by reacting known excess of **1** with known deficient amount of the reductants and calculating the equilibrium absorbance values.

## RESULTS AND DISCUSSION

### Stoichiometry and the reaction products

With excess [**1**], spectrophotometric determination of the residual [**1**] indicated a 1:2 stoichiometry ( $\Delta[\text{PhCH}_2\text{OH}]:\Delta[\text{1}]$ ). This stoichiometry suggest that the reaction product of  $\text{PhCH}_2\text{OH}$  is benzaldehyde and it was confirmed by Tollens' and Fehling's reagent tests. The final solution after determination of stoichiometry gave a positive Tollens' reagent test but a negative Fehling's test confirming the formation of aromatic aldehyde<sup>9</sup> Similar determination with 2-propanol also indicated 1:2 stoichiometry ( $\Delta[2\text{-prpanol}]:\Delta[\text{1}]$ ), hence the reaction product of 2-propanol is acetone, confirmed by 2,4-dinitrophenylhydrazine test.<sup>9</sup> **1** undergoes reduction to its most common reduction product  $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{HO}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$  (**2**).<sup>10</sup> Based on spectral observations, it is established that the reduction of **1** by divalent metal ions like  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$  and  $\text{Eu}^{2+}$  in acid media results in a protonated structure for the intermediate peroxo complex (**2**). **2** quickly decomposes to  $\text{Co(II)}$ ,  $\text{NH}_3$  and  $\text{O}_2$ <sup>8,10</sup> and did not affect the overall kinetics. Independent experiments showed that the products benzaldehyde and acetone did not react with **1**. Hence the overall reaction is represented by eqns 1 and 2, which are followed by the rapid decomposition of **2**.



(1)

(2)



(1)

(2)

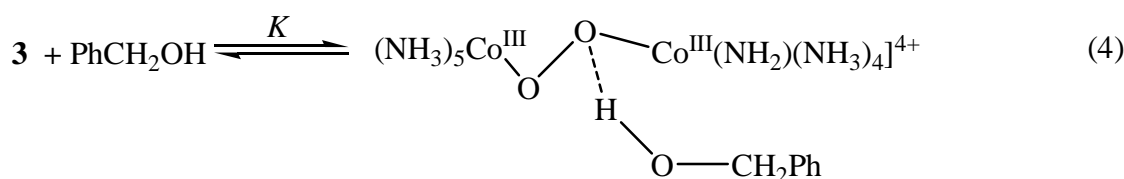
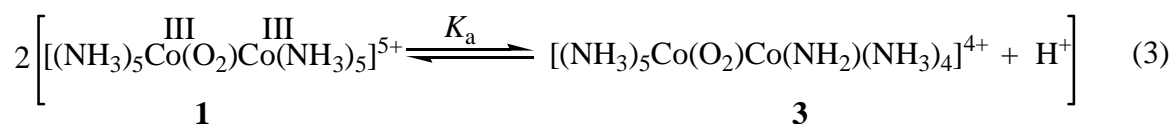
$\text{CH}_3\text{COCH}_3$  (2)

### Kinetics and Mechanism

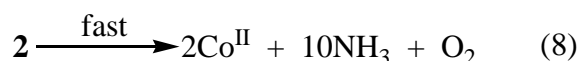
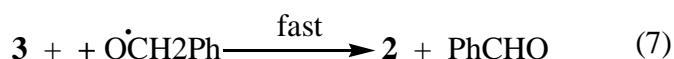
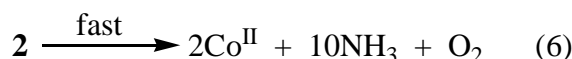
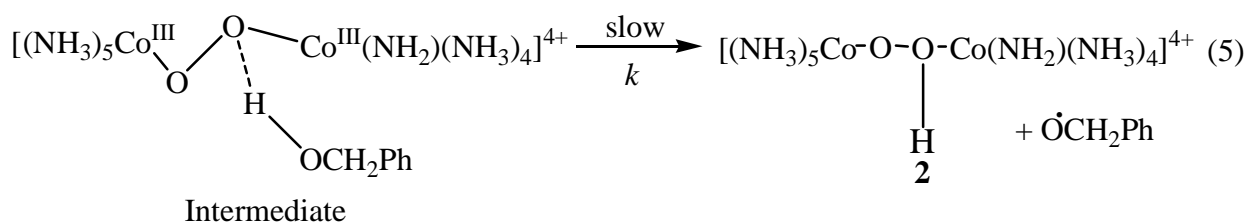
Under the reaction conditions,  $\text{PhCH}_2\text{OH}$  and 2-propanol slowly consumed **1**, reducing the absorbance with time, and the process followed excellent first-order kinetics. A family of time-resolved spectra describing such changes is shown in Fig. 1. The first-order rate constants,  $k_o$  increased linearly with [alkanol] (Table 1 and 2, Fig 2 and 3) in the entire pH range studied.  $k_o$  and

exhibited prominent inverse proton dependence (Table 1 and 2). Neither the buffer concentration nor the media ionic strength had any significant effect on the observed rate.

The fact that the rate is unmistakably enhanced with pH seems not accountable from deprotonation of reductants. Both PhCH<sub>2</sub>OH and 2-propanol are too weak an acid (pK<sub>a</sub> of PhCH<sub>2</sub>OH = 15.40 and pK<sub>a</sub> of 2-propanol = 16.5)<sup>11</sup> to deprotonate in the working pH range. The observed inverse proton dependence could not be traced at the superoxo moiety in **1** either because the superoxo coordinated to **1** has no dissociable proton. So the only possibility is dissociation of an H<sup>+</sup> ion from one of the coordinated NH<sub>3</sub> molecules in **1**, thus forming a conjugate base [(NH<sub>3</sub>)<sub>5</sub>Co(O<sub>2</sub>)Co(NH<sub>3</sub>)<sub>4</sub>(NH<sub>2</sub>)]<sup>4+</sup> (**3**) as the kinetically reactive species. **1** is susceptible to decompose in neutral and in basic media, so a base hydrolysis path, through **3** is available to **1**<sup>12</sup> These kinetic observations suggest that the oxidation of PhCH<sub>2</sub>OH and 2-propanol by **1** occurs *via* steps (3)–(8) below:



H-bonded adduct (Intermediate)



Scheme 1

Scheme 1 leads to eqn. (9).

$$k_{\text{obs}}/[\text{alkanol}] = kKK_a/[\text{H}^+] \quad (9)$$

A plot of  $k_{\text{obs}}/[\text{alkanol}]$  versus  $1/[\text{H}^+]$  (eqn. 9) yielded excellent straight line with a statistically insignificant intercept (Fig. 3 and 4 for PhCH<sub>2</sub>OH and for 2-propanol).

## ACKNOWLEDGEMENTS

Department of Chemistry, Jadavpur University is thankfully acknowledged for instrumental facilities.

## REFERENCES

1. Jones CM, Burkitt MJ, J. Am. Chem. Soc. 2003, 125, 6946-6954.
2. (a) Commenges D, Scotet V, Renaud S, Jacqmin-Gadda H, Barberger-Gateau P, Dartigues JF., Eur. J. Epidemiol. 2000; 16: 357-363; (b) Whitehead T P, Robinson D, Allaway S, Syms J, Hale A, Clin. Chem. 1995; 41: 32-35; (c) Hertog MGL, Feskens EJM, Hollman PCH, Katan MB, Kromhout D, Lancet 1993; 342: 1007-1011.
3. Lippard SJ, Berg JM, Principles of Bioinorganic Chemistry (University Science Books, Mill Valley, CA) 1994; (b) Sono M, Roach MP, Coulter ED, Dawson JH, Chem. Rev. 1996; 96, 2841-2887; (c) Ferguson-Miller S, Babcock GT, Chem. Rev. 1996; 96: 2889-2907; (d) Blackman AG, Tolman WB, Struct. Bonding 2000; 97: 179-211; (d) Costas M, M. Mehn P, Jensen MP, Que, Jr L Chem. Rev. 2004; 104: 939-986.
4. (a) Fridovich I, Acc. Chem. Res. 1972; 5: 321-326; (b) Fridovich I, Adv. Inorg. Biochem. 1979; 1: 67-90; (c) Fee JA, Valentine JS, In Superoxide and Superoxide Dismutase; A. M Michelson, J. M. McCord, I. Fridovich, Eds.; Academic Press: New York, 1979; 19.
5. (a) Filippo, Jr JS., Chern CI, Valentine JS, J. Org. Chem. 1975; 40: 1678-1680; (b) Gibian, MJ, Sawyer DT, Ungermann T, Tangpoonpholvivat R, Morrison MM, J. Am. Chem. Soc. 1979; 101: 640-644.
6. Davies R, Mori M, Sykes AG, Weil, J.A, Inorg. Synth, 1982; 12: 197.
7. Saha SK, Ghosh MC, Gould ES, Inorg. Chem. 1992; 31: 5439.
8. Hoffman AB, Taube H, Inorg. Chem. 1968; 7: 1971-1976
9. Vogel's Textbook of Practical Organic Chemistry, Ed. Brian S. Furniss, Pearson, 5<sup>th</sup> Edition, 2006;1219.
10. Ghosh SP, Saha SK, Bose RN, Reed JW, Ghosh MC, Gould ES, Inorg. Chem. 1993; 32: 2261-2264.
11. Reeve W, Erikson CM, Aluotto PF, Can. J. Chem. 1979; 57: 2747-2754.

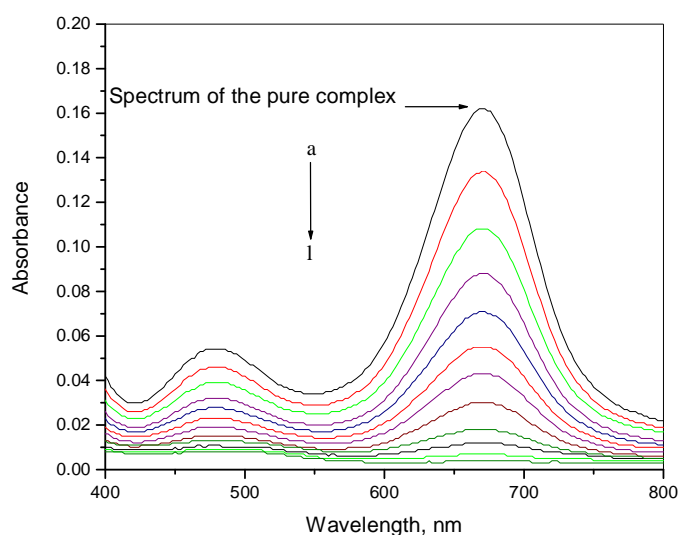
12. a) Mishra R, Mukhopadhyay S, Banerjee R, Dalton Trans. 2009; 5469-5473; b). Mandal K, Banerjee R, Dalton Trans., 2012; 41: 2714-2719.

**Table 1. Some representative first-order rate constants ( $k_o$ ) for the reduction of 1 (0.20 mM) by PhCH<sub>2</sub>OH,  $I = 0.50$  M (NaClO<sub>4</sub>),  $T = 25.0$  °C.**

[PhCH <sub>2</sub> OH], M	pH	$10^3 k_o, s^{-1}$
0.02	4.70	1.2
0.02	4.95	1.95
0.02	5.12	3.05
0.02	5.3	4.01
0.02	5.45	5.6
0.02	4.70	1.2
0.04	4.70	2.2
0.06	4.70	3.2
0.08	4.70	4.1
0.1	4.70	5.3

**Table 2. Some representative first-order rate constants ( $k_o$ ) for the reduction of 1 (0.20 mM) by 2-propanol,  $I = 0.50$  M (NaClO<sub>4</sub>),  $T = 25.0$  °C.**

[2-propanol], M	pH	$10^3 k_o, s^{-1}$
0.02	4.7	0.15
0.02	4.90	0.25
0.02	5.10	0.40
0.02	5.30	0.53
0.02	5.45	0.73
0.02	4.90	0.25
0.04	4.90	0.29
0.06	4.90	0.41
0.08	4.90	0.53
0.1	4.90	0.68



**Figure 1. Time-resolved spectra of 0.20 mM of 1 reacting with 0.02M PhCH<sub>2</sub>OH. pH = 4.70 in acetate buffer ( $T_{OAc} = 0.20$  M),  $I = 0.50$  M (NaClO<sub>4</sub>),  $T = 25.0$  °C.. (a): spectrum of pure complex shown in black; (b) – (l): spectra of reaction mixtures.**

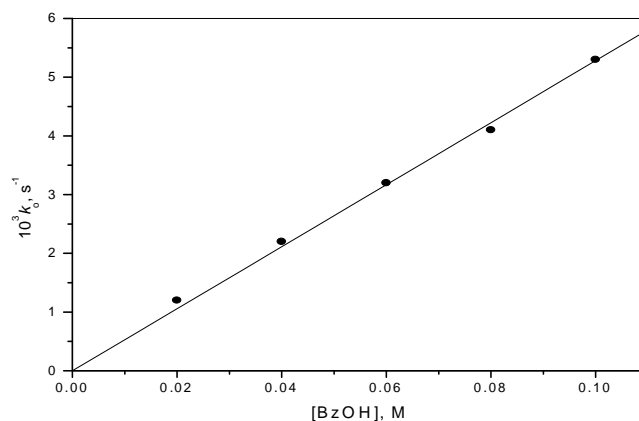


Figure 2. Variation of  $k_0$  with [PhCH<sub>2</sub>OH]. [1] = 0.20 mM, pH = 4.70 ( $T_{OAc}$  = 0.20 M),  $I$  = 1.0 M (NaClO<sub>4</sub>),  $T$  = 25.0 °C.

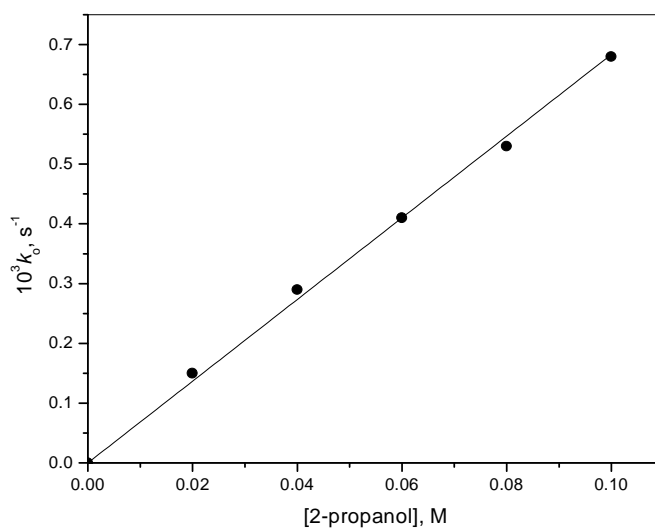


Figure 3. Variation of  $k_0$  with [2-propanol]. [1] = 0.20 mM, pH = 4.90 ( $T_{OAc}$  = 0.20 M),  $I$  = 1.0 M (NaClO<sub>4</sub>),  $T$  = 25.0 °C.

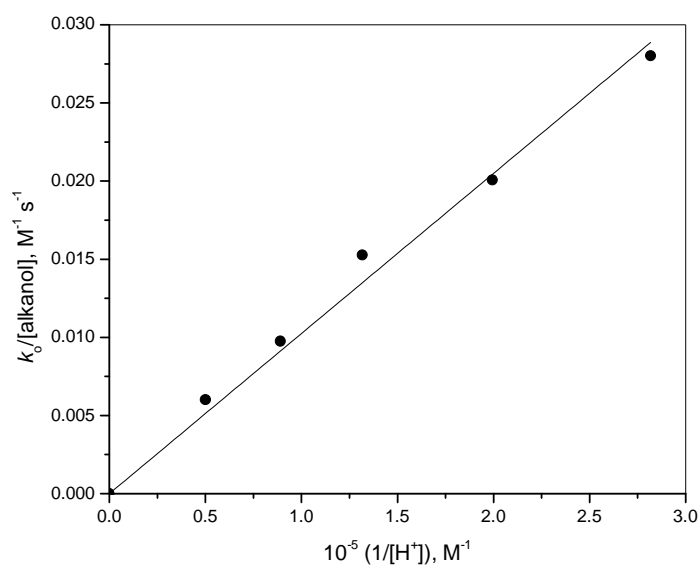


Figure 4. Variation of  $k_0/[\text{alkanol}]$  with  $1/[\text{H}^+]$ ,  $[\text{I}] = 0.20 \text{ mM}$ ,  $[\text{PhCH}_2\text{OH}] = 0.2 \text{ M}$ ,  $(\text{T}_{\text{OAc}} = 0.20 \text{ M})$ ,  $I = 1.0 \text{ M}$  ( $\text{NaClO}_4$ ),  $T = 25.0 \text{ }^\circ\text{C}$ .

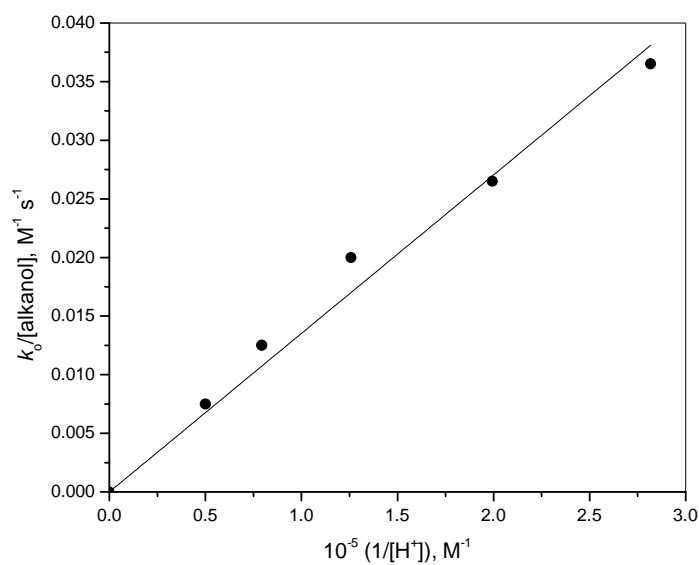


Figure 5. Variation of  $k_0/[\text{alkanol}]$  with  $1/[\text{H}^+]$ ,  $[\text{I}] = 0.20 \text{ mM}$ ,  $[\text{2-propanol}] = 0.02 \text{ M}$ ,  $(\text{T}_{\text{OAc}} = 0.20 \text{ M})$ ,  $I = 1.0 \text{ M}$  ( $\text{NaClO}_4$ ),  $T = 25.0 \text{ }^\circ\text{C}$ .