

KINETIC STUDY OF THE REACTION OF 2,2'-BIPYRIDYL CHROMIUM PEROXIDE WITH ALCOHOLS

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Abstract

The rate constants and activation parameters are reported for the oxidation of methanol, ethanol, propanol, and isopropanol by 2,2'-bipyridyl chromium peroxide (BPCP) over the temperature range of 35° to 50°C.

Introduction

The oxidation of alcohols with chromium peroxide complexes has been investigated extensively [1-5]. These complexes have interesting properties such as reasonable stability, operational simplicity, solubility in organic solvents, easy workup and particularly high yields. For example, benzyl alcohol was converted to benzaldehyde in high yields. Hydroquinone, catechol and 1,4-dihydroxy naphthalene were oxidized very easily to their quinines [2].

The mechanism of reaction of 3,4-lutidine chromium peroxide (LCP) with ethanol was studied [6]. It was suggested that the ligand exchange stage is the rate determining step and the peroxide linkage is primarily responsible for the oxidation process.

We were interested in studying the influence of the ligand structure on the kinetics of the oxidation of alcohols by different chromium peroxide complexes. In this paper, 2,2'-bipyridyl chromium peroxide, which has a larger bidentate ligand was used and the kinetic behaviour of this oxidizing reagent with simple alcohols such as methanol, ethanol, propanol, and iso-propanol were also studied.

Keywords: Alcohols; BPCP; Kinetics; Oxidation; Spectrophotometry

2,2'-Bipyridyl chromium peroxide was prepared by the addition of 2,2'-bipyridyl to ethereal solution of chromium (VI) peroxide. This reagent, which has a general structure of $\text{Bipy.CrO}(\text{O}_2)_2$ [7,8], reacts with alcohols to give the corresponding carbonyl compounds as products. The crystalline structure of BPCP has been reported in this paper [9,10].

Experimental Section

Materials

2,2'-Bipyridyl chromium peroxide (BPCP) was prepared according to the reported procedure [7]. Reagent grade methanol (MeOH), ethanol (EtOH), propanol (PrOH), and isopropanol (i-PrOH) were purchased from Merck Chemical Company and used without further purification.

Kinetic Experiments

The reaction were carried out in a homogeneous alcohol solution of 2,2'-bipyridyl chromium peroxide (usually ca. 0.5 mg of BPCP in 5 ml of alcohol) [11] and a pseudo first-order behaviour for these reactions were followed spectrophotometrically using a GBC Model 911 spectrophotometer. Rate coefficients were evaluated from the absorbance of the reaction solution measured at a wavelength 650 nm against time.

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Product Analysis

The organic products of the oxidation of alcohols with BPCP are corresponding carbonyl compounds [2] and were identified with a Gow-Mac gas chromatography, equipped with a 10% carboxpack column. Nitrogen was used as carrier gas with thermal conductivity detector. The injection part and detector temperature were maintained at 140° and 120°C, respectively.

Results and Discussion

The reactions were followed by the disappearance of the visible absorption of BPCP at about 650 nm. The first-order rate coefficients, k_1 , were obtained from absorbance data collected over at least 75% of the reaction and evaluated from the integrated rate equation. The rate constant k_1 , calculated for all reactions at various temperatures, are summarized in Table 1.

Arrhenius energy plots are shown in Figure 1. By using Eyring's Equation [12], the least squares plots of $\ln(k_1/T)$ vs. $1/T$ (Fig. 2) were used to evaluate the activation parameters ΔH^\ddagger and ΔS^\ddagger , in which case ΔG^\ddagger has been calculated at 35°C.

It is obvious that two significant features emerge from the results given in Table 1. The first notable feature is that the pseudo first-order rate constants vary in the order $\text{PrOH} > \text{i-PrOH} > \text{n-EtOH} > \text{MeOH}$. According to the theory of absolute reaction rates, the reactant basicity and the solvent polarity can be assumed to affect the kinetic behaviour of the system. The basicity of alcohols, indicated by the β -value of Kamlet, Taft and coworkers [13,14] is in the order of

$\text{i-PrOH} > \text{PrOH} > \text{EtOH} > \text{MeOH}$. Therefore, it seems reasonable to assume that the presence of the bulkier i-PrOH, in the transition state, introduces more steric hindrance which should be the cause of the unexpected lower reaction rate for this alcohol.

Moreover, it is seen that a decrease in the solvent polarity reflected in its dielectric constant ϵ and Kosowers Z-values [15], seems to facilitate increasing the stability constant of the intermediate complex in the ligand exchange process which leads to a decrease in the activation barrier. These results indicate that the transition state should be less polar than the initial reactants as was previously pointed out [6].

The second significant point is that the range of the reactivity of alcohols used with BPCP is remarkably small (i.e. less than 10 at any temperature). This is, in part, a consequence of compensating changes in activation energy and entropy (Fig. 3) [12]. For example, n-PrOH, with the lowest ΔH^\ddagger , has the most negative ΔS^\ddagger and EtOH with the highest ΔH^\ddagger , has the least negative ΔS^\ddagger (Table 1). In other words, while both ΔS^\ddagger and ΔH^\ddagger values decrease to more negative values with decreasing the solvent polarity, the change in the free energy of activation ΔG^\ddagger will remain more or less the same.

Comparison of the rate constants for the reaction of methanol with BPCP and chromium peroxide etherate (CPE) [11], shows the higher rate constant for CPE reaction. 2,2'-Bipyridyl as a soft donating ligand is expected to form the strongest complex with chromium peroxide as a soft acid [16] than diethylether as a hard donating ligand.

Table 1. Pseudo-first-order rate constants at different temperatures and the activation parameters for the decomposition of 2,2'-bipyridyl chromium peroxides in various alcohols

Alcohol	MeOH		EtOH		n-PrOH		i-PrOH	
	$K_{\text{obs}} \times 10^3 \text{ (sec}^{-1}\text{)}$	(r)	$K_{\text{obs}} \times 10^3 \text{ (sec}^{-1}\text{)}$	(r)	$K_{\text{obs}} \times 10^3 \text{ (sec}^{-1}\text{)}$	(r)	$K_{\text{obs}} \times 10^3 \text{ (sec}^{-1}\text{)}$	(r)
308	0.49±0.04	(0.9991)	0.53±0.04	(0.9994)	1.14±0.04	(0.9992)	0.76±0.06	(0.9987)
313	0.86±0.03	(0.9983)	0.98±0.03	(0.9995)	1.67±0.01	(0.9998)	1.39±0.02	(0.9997)
318	1.56±0.02	(0.9976)	1.81±0.01	(0.9988)	2.60±0.02	(0.9991)	2.28±0.03	(0.9996)
323	2.87±0.03	(0.9985)	2.90±0.01	(0.9970)	4.49±0.02	(0.9902)	3.92±0.02	(0.9962)
E_a (KJ/mol)	97.5	(0.9994)	94.6	(0.9988)	75.0	(0.9955)	89.4	(0.9962)
ΔH^\ddagger (KJ/mol)	94.9	(0.9994)	91.9	(0.9987)	72.4	(0.9955)	86.9	(0.9995)
ΔS^\ddagger (KJ/mol)	-0.6		-9.3		-66.9		-22.7	
ΔG^\ddagger (KJ/mol)	95.1		94.8		93.0		93.9	
Value β	0.61		0.77		0.78		0.92	
Value Z	83.6		79.6		78.3		76.3	
ϵ	32.7		34.6		20.3		19.9	

Conclusion

The pseudo-first-order rate constants for the oxidation of the alcohols used with BPCP vary in the order $\text{PrOH} > \text{i-PrOH} > \text{EtOH} > \text{MeOH}$. The range of reactivity of the alcohols is significantly small, which is partly due to the observed compensating change.

Acknowledgements

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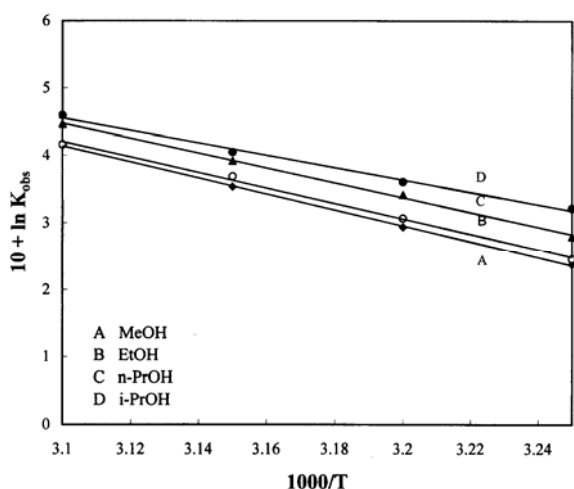


Figure 1. Arrhenius activation plots of $\ln k_1$ vs. $1/T$ for the decomposition of BPCP in various alcohols.

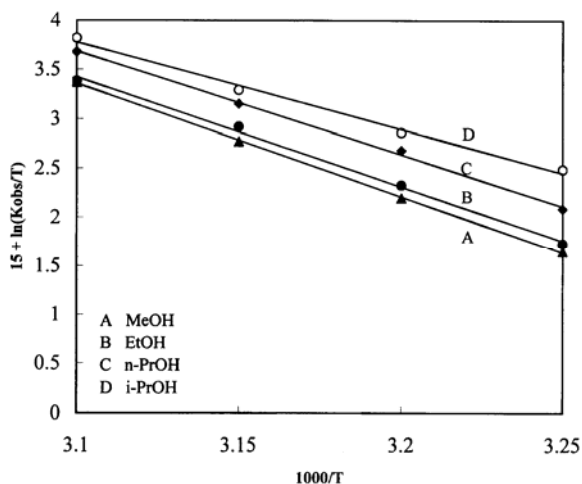


Figure 2. Plots of $\ln(k_1/T)$ vs. $1/T$ for the decomposition of BPCP in various alcohols.

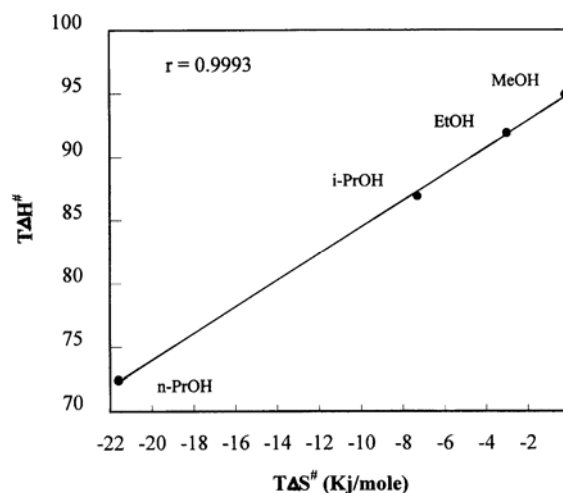


Figure 3. Plots of ΔH^\ddagger vs. $T\Delta S^\ddagger$ for the decomposition of BPCP in various alcohols.

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