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A KINETIC STUDY OF THE DECOMPOSITION OF PYRIDINE CHROMIUM (VI) PEROXIDE WITH ALCOHOLS

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Abstract

A kinetic study of the decomposition of pyridine chromium peroxide with methanol, ethanol, propanol and isopropanol has been made over the temperature range 25 to 40°C. It is found that the ligand exchange stage is the rate determining step in the oxidation process. The activation parameters E_a, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the reactions are determined. It is believed that the peroxide linkage is primarily responsible for the oxidation process.

Introduction

The addition of hydrogen peroxide to an acidic chromate solution results in a blue chromium (VI) peroxide which can be extracted with diethyl ether to give a relatively stable compound. The etherial solution reacts with electron-pair donating substances such as pyridine (Py) to form a deep-blue pyridine chromium peroxide (PCP) having a general structure of $PyCr(0)(0_2)_2$ [1]. The crystalline structure of PCP has been reported in the literature [2,3]. In the solid state, the chromium atom, the two peroxy groups and the nitrogen atom of pyridine are all nearly coplanar, while the fifth oxygen atom lies above the central chromium atom.

The successful use of the chromium peroxide complexes as an attractive possibility for the mild oxidation of a variety of organic compounds has already been reported [4-8]. It is believed that, because of their interesting properties, such as solubility in organic solvents, reasonable stability, operational simplicity, easy workup and, in particular their high yields, chromium peroxide complexes will find widespread applications in organic synthesis.

Despite the high applicability of chromium peroxides, the mechanism of their oxidation reactions remains unclear at the present time. It is not clear yet whether the peroxo oxygens, the chromium (VI) or both of them are responsible for the oxidation processes. However, the kinetics of the system can be expected to be complex due, at least in part, to the possible existence of more than one pathway for the decomposition of chromium peroxides. In this study, attempts were made to gain an insight into the kinetic behavior and the mechanism of the oxidation of organic compounds by chromium peroxides. This paper presents a study of the decomposition kinetics of PCP in methanol, ehtanol, propanol and isopropanol solutions.

Keywords: Pyridine chromium peroxide; 4-Acetylpyridine chromium peroxide; Chromium peroxide etherate ; Alcohol; Decomposition kinetics; Oxidation; Spectrophotometry

Experimental Section

Reagents

Chromium peroxide etherate (CPE), pyridine chromium peroxide (PCP) and 4-acetylpyridine chromium peroxide (APCP) were prepared by the previously reported methods [5]. Methanol (MeOH), ethanol (EtOH), propanol (PrOH) and isopropanol (i-PrOH), all of Fluka A.G. quality, were used without any further purification.

Kinetic Measurements

About 5ml of the alcohol was separately thermostated at the desired temperature (± 0.1°C) for about 1h. The reaction was started by the addition of a given amount

(~0.5mg) of PCP to the alcohol. The mixing time was kept as short as possible. The decomposition kinetic of PCP was followed by the absorbance measurement of the solution at a convenient wavelength (usually 565nm) against time. The visible absorption spectra were recorded with a Beckman DK-2A ratio recording spectrophotometer and the absorbance measurements were made by using a Cary Model 118 spectrophotometer. Silica cells of 1.0cm thickness were employed.

Product Analysis

The organic products of the oxidation reactions of alcohols used with PCP were identified with gas chromatography and ^{1}H NMR techniques. A Gow-Mac gas chromatograph equipped with a 10% carbopak column was used. NMR measurements were made on a model R-24B, 60 MHz Hitachi instrument using TMS as internal standard.

Results

Kinetic Studies

The disappearance of the PCP band at about 565 nm and the formation of the product band at about 360 nm was followed by time. Figure 1 shows the changes in these bands in a typical kinetic run. The existence of a well-defined isobestic point at 467 nm indicates that the absorbance is due nearly entirely to reactant and product. The same spectral behavior was observed for all systems studied. Pseudo-first-order conditions were maintained in all runs by the use of a large excess of alcohols over PCP. Thus, semi-logarithmic plots of the residual PCP contents as a function of time were found to be linear to a degree of completion of two half-lives or more (see Fig. 2 as an example). The pseudo-first-order rate constants k_1, calculated from the slope of such plots for all cases studied at different temperatures, are given in Table 1.

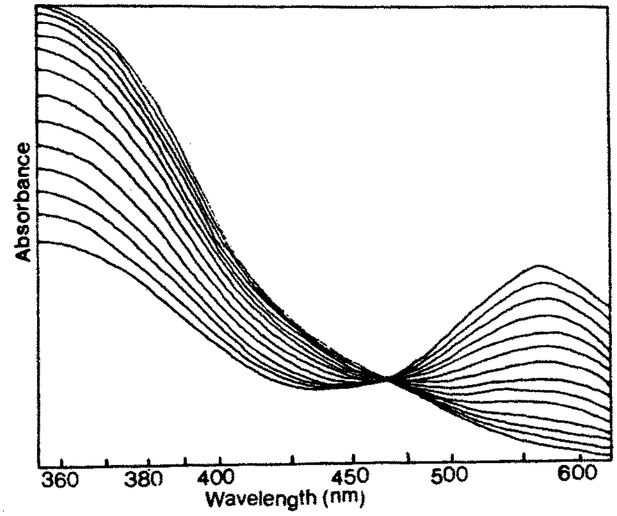

Figure 1. Visible spectra resulting from a kinetic run for the decomposition of PCP in EtOH at 25°C. Time intervals = 2mins.

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

Oxidizing	Alcohol	ε	Z-value	β-value	$k_1 \times 10$ (min^{-1}) 25°	30°	35°	40°	E_a (kj mol^{-1})	$\Delta G^{\ddagger}$ (kj mol^{-1})	$\Delta H^{\ddagger}$ (kj mol^{-1})	$\Delta S^{\ddagger}$ (jk^{-1} mol^{-1})
CPE	MeOH	32.7	83.6	0.61	1.365	2.228	2.965	3.518	48.7	77.8	46.2	-105.8
					(0.062)	(0.052)	(0.073)	(0.081)	(0.7)	(3.2)	(0.7)	(3.1)
APCP					0.738	1.186	1.276	1.957	49.6	54.7	47.1	-25.5
					(0.007)	(0.023)	(0.008)	(0.077)	(1.0)	(1.8)	(1.0)	(1.5)
PCP					0.178	0.709	1.560	3.240	147.7	82.8	145.2	208.4
					(0.005)	(0.018)	(0.041)	(0.079)	(1.8)	(6.3)	(1.8)	(6.0)
	EtOH	24.6	79.6	0.77	0.329	0.954	1.720	3.510	119.7	81.6	117.2	119.7
					(0.011)	(0.092)	(0.170)	(0.390)	(1.1)	(3.9)	(1.2)	(3.7)
	PrOH	20.3	78.3	0.78	2.140	4.550	7.590	15.840	101.2	77.0	98.7	73.2
					(0.074)	(0.270)	(0.390)	(0.191)	(2.11)	(2.0)	(0.6)	(1.9)
	i-PrOH	19.9	76.3	0.92	0.893	1.637	2.452	3.980	75.3	79.1	72.8	-20.9
					(0.056)	(0.143)	(0.200)	(0.390)	(1.4)	(1.5)	(0.4)	(1.4)

The values in parentheses show errors associated with kinetic parameters in ± standard deviations.

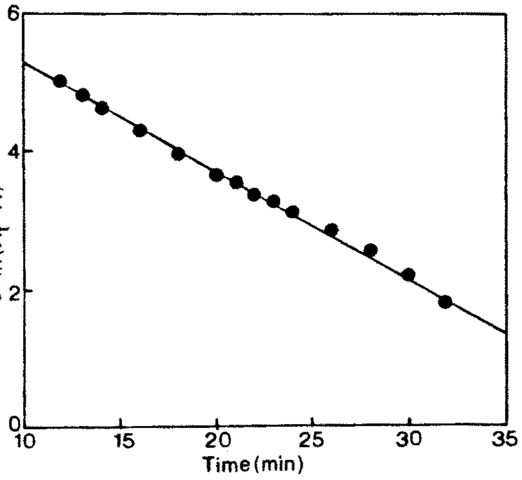

Figure 2. Pseudo-first-order plots for the decomposition of PCP in MeOH at 35°C

Effect of Temperature

The decomposition kinetics of PCP in the alcohols used was studied at four different temperatures (Table 1). Arrhenius energy plots, log k_1 vs. 1/T, are shown in Figure 3. The activation energy can be determined from the slope of these plots. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been calculated by using Eyring's transition-state theory [9]:

$$\ln\frac{k_1}{T}=\left(\ln\frac{k}{h}+\frac{\Delta S^\ddagger}{R}\right)-\frac{\Delta H^\ddagger}{RT} \qquad (1)$$

The least squares plots of ln k_1/T vs. 1/T (Fig. 4) were used to evaluate the enthalpy and entropy of activation. The results of these calculations are also included in Table 1.

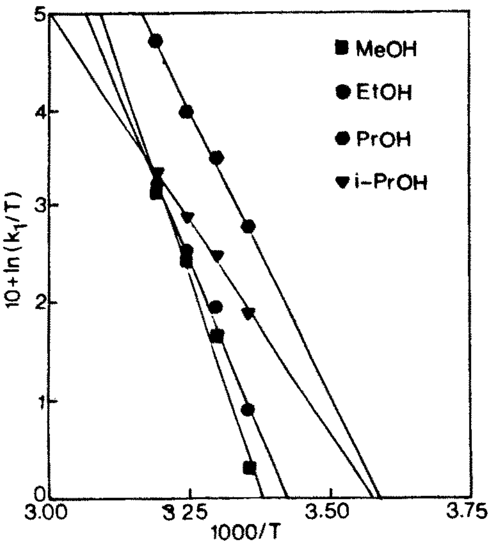

Figure 4. Plots of ln (k_1/T) vs. 1/T for the decomposition of PCP in various alcohols

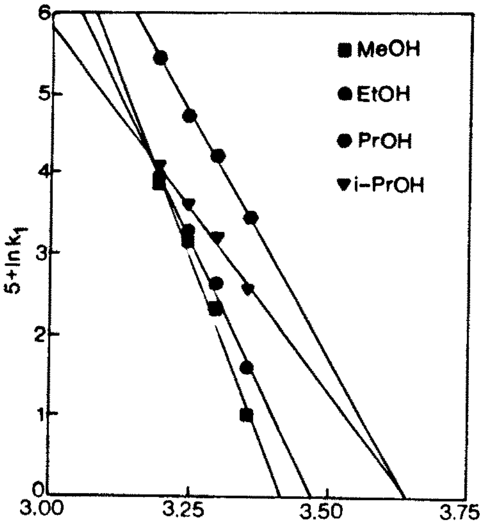

Figure 3. Arrhenius activation plots of ln k_1 vs. 1/T for the decomposition of PCP in various alcohols

Products of the Oxidation Reactions

In this study, acetone as an oxidation product of i-PrOH with PCP was identified by gas chromatography and ^{1}H NMR. The amount of acetone produced as a function of reaction time is given in Figure 5. The gas chromatographic data for acetone was used to examine the stoichiometry of the reaction between PCP and i-PrOH. It was found that PCP can convert the alcohol into acetone in good yield (> 90%) [5] according to a 2:1 stoichiometry (alcohol to PCP) [7,8].

As is seen from Figure 1, the final solution is a yellow-brown solution which absorbs light at a λ_{max} of about

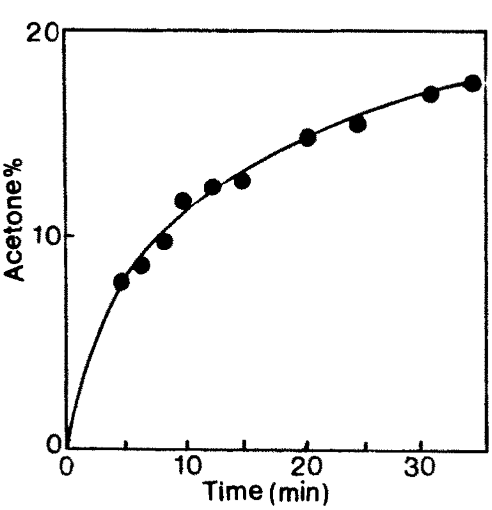

Figure 5. Rate of formation of acetone in the PCP oxidation of i-PrOH at 25°C

360nm. The spectral characteristics of the solution nicely match those reported by Wiberg and Mukherjee for Cr (VI) in the chromic acid oxidation of isopropanol [10]. The presence of Cr (VI) in the final solution, probably as CrO_3, was also confirmed by the formation of a yellow precipitate of $PbCrO_4$ upon addition of a saturated aqueous solution of lead acetate to the reaction medium [11].

It should be noticed that, after the complete disappearance of the 565nm band (i.e complete decomposition of PCP), the absorbance of the product band at 360 nm was found to decrease slowly with time. Thus, it is reasonable to assume that after the complete conversion of PCP to CrO_3 in the first step, the oxidation of the alcohol will be continued by the reduction of chromium (VI) to its lower oxidation states. Oxidation of alcohols with Cr (VI), as chromic acid, in acidic medium has been investigated extensively [10, 12-15].

Discussion

From Table 1 it can be seen that the rate constants for the oxidation of methanol with various chromium peroxide complexes vary in the order CPE > APCP > PCP. Because of the soft character of the nitrogen atom, pyridine is expected to form a stronger complex with chromium peroxide (as a soft acid) [16] than diethyl ether, as a hard donating ligand. On the other hand, the introduction of an electron withdrawing group, such as the acetyl group, to the para position of pyridine reduces the electron-pair density of this ligand and, hence, a weaker complex results. Consequently, the trend observed in the decomposition rate of various chromium peroxides in methanol strongly emphasizes the existence of a ligand exchange process (between the reacting alcohol and the previously attached ligand) as the bottleneck step in the corresponding oxidation reactions [8].

Thus, based on the spectral behavior observed and the kinetic data obtained in this study, the reactions between PCP and the alcohols under study are believed to proceed via a slow formation of an intermediate, during a ligand exchange process. Subsequently, fast oxidation of the alcohols by the peroxo groups of PCP to the corresponding aldehydes or ketones occur.

From Table 1 it is obvious that, at all temperatures studied, the pseudo-first-order rate constants for the oxidation of alcohols by PCP vary in the order PrOH > i-PrOH > EtOH > MeOH. According to the theory of absolute reaction rates [9], two important parameters can be assumed to affect the kinetic behavior of the system, namely, the solvent polarity and the reactant basicity. A decrease in the solvent polarity, reflected in its dielectric constant ε and Kosower's Z-values [17], seems to increase the stability constant of the intermediate complex, in the ligand exchange process, and this leads to a decrease in the activation barrier. However, the basicity of alcohols, indicated by the β-value of Kamlet, Taft and coworkers [18,19] is in the order of i-PrOH > PrOH > EtOH > MeOH. Therefore, it seems reasonable to assume that the presence of the bulkier i-PrOH in the transition state introduces more steric hinderance which should be the cause of the unexpected lower reaction rate of this alcohol.

It is interesting to note that, while both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values decrease (to more negative values) by an increase in the solvent polarity, the change in the free energy of activation $\Delta G^{\ddagger}$ will remain more or less the same, the so-called "compensation effect" (Fig. 6) [9]. This is also in confirmity with the above-mentioned solvent effect, and reflects the much lower polarity of the transition state complex in comparison with PCP as the initial reactant.

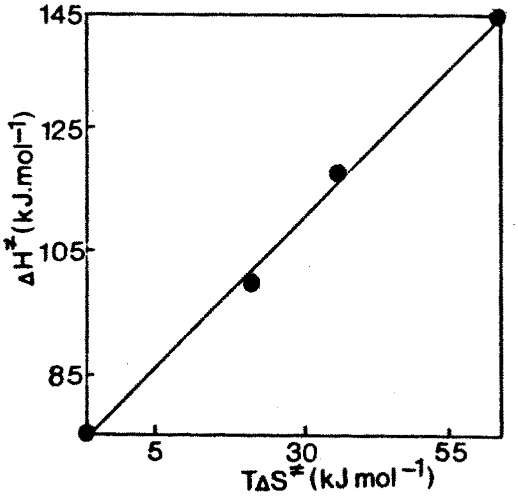

Figure 6. plot of $\Delta H^{\ddagger}$ vs. $T\Delta S^{\ddagger}$ for the decomposition of PCP in various alcohols

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