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THERMAL AND ELECTRON PARAMAGNETIC RESONANCE STUDIES ON PYRIDINE PERCHROMATE

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ABSTRACT

A number of physical techniques including scanning calorimetry and electron paramagnetic resonance have been used in an attempt to elucidate the course of the decomposition reaction of pyridine perchromate.

Kinetic parameters have been obtained and comments are made on their unusual magnitudes.

INTRODUCTION

Pyridine perchromate, $CrO_5(py)$ (py = pyridine) can be isolated as a deep blue solid with the structure[1] shown in Fig. 1. Previous studies on the solid compound have been of a qualitative nature, showing it to be thermally unstable and that aged samples may explode violently, even at room temperature[2].

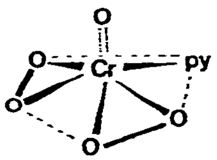

Fig. 1. The structure of pyridine perchromate.

Rai and his co-workers have studied the decomposition of perchromic acid and its derivatives in solution[3-5]. A first order decomposition was observed with a marked induction period at low temperatures[3].

We chose to study the decomposition of the solid complex and to obtain calorimetric and kinetic data in order that the thermal instability of the compound could be better understood.

The calorimetric measurements required the use of a differential scanning calorimeter since a small sample size and a slow heating rate may be used, thus preventing explosive decompositions.

The isothermal, room-temperature decomposition was studied by EPR. This technique has been previously employed in inorganic reaction kinetics studies[6]. In many of these studies it is necessary to use a specially constructed spectrometer with rapid recording instrumentation to detect the short-lived paramagnetic species[7,8]. A conventional spectrometer may, however, be used in the study of longer-lived species and pyridine perchromate was, therefore, suitable since it was known that the decomposition half-life was considerable[4].

EXPERIMENTAL

Calorimetry

A Perkin-Elmer Differential Scanning Calorimeter (DSC-1B) was used for the calorimetric measurements. All decompositions were carried out under dry nitrogen. Sample encapsulation and other details of the calorimetric procedure were as previously described[9]. Small sample sizes (< 5 mg) and slow heating rates were employed to prevent explosive decompositions.

The curves obtained from the calorimeter were treated in a manner similar to that previously described[10] to obtain a least squares solution for the parameters A, E, and n in the equation

$$\frac{d\alpha}{dt} = A \cdot \exp(-E/RT) \cdot (1-\alpha)^n$$

where

α = extent of decomposition

$\frac{d\alpha}{dt}$ = rate of decomposition at temperature T

E = activation energy

n = an average value of the "order of reaction"[11]

A = the Arrhenius pre-exponential factor.

The ICL 1903A computer at this Polytechnic was used in the solution of these equations. The experimental and computed rates were exhibited graphically on a digital plotter. This permitted a rapid visual check on the validity of the calculations.

Provision has been made in this revised program* to avoid ill conditioned solutions which may result from certain experimental conditions[12].

EPR studies

EPR measurements were made on the solid metal complex at room temperature with a Hilger and Watts "Microspin" spectrometer operating at X-band frequences. The Kystron frequency was locked to the resonant frequency of the sample cavity so

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*A copy of the program, in FORTRAN IV, including the plotter subroutine is available from the authors.

that pure absorption was recorded and the frequency was measured with a wavemeter. The microwave power incident on the sample cavity was approximately 20 mW.

Phosphorus-doped silicon was used as a *g*-marker[13] and marker pips for magnetic field strength calibration were added with a proton resonance magnetometer system.

We have taken the signal amplitude to be proportional to the number, N, of paramagnetic species and this is justified by the Eqn. (1)[13] in cases where the line width or lineshape of the EPR signals do not change.

$$N_x = \left(\frac{H_{ms}}{H_{mx}}\right)\left(\frac{\Delta H_x}{\Delta H}\right)^2\left(\frac{A_x}{A}\right)\left(\frac{G_s}{G_x}\right)\left(\frac{H_{0s}}{H_{0x}}\right)N_s \qquad (1)$$

where

S refers to silicon
X refers to the sample
H_m = modulation amplitude
ΔH = line width
A = signal amplitude
G = gain of complete system
H_0 = magnetic field at centre of line

Infrared spectroscopy

IR spectra of KBr discs were recorded on a Perkin–Elmer 457 spectrometer between 650 and 4000 cm^{-1}.

Mass spectrometry

Mass spectra of the solid compounds were obtained with the direct insertion probe of a Hitachi Perkin–Elmer RMU-6 spectrometer.

Preparations

Pyridine perchromate was prepared by a standard procedure[14] and gave satisfactory microanalytical results (Found: C, 29.3; H, 2.6; N, 6.5%. Calc.: C, 28.4; H, 2.4; N, 6,6%).

We also attempted to prepare stable derivatives of other organic bases. These were insufficiently stable for our investigations, and, in some cases (for example, with 2-methylpyridine) could not be isolated.

RESULTS AND DISCUSSION

IR and mass spectrometric measurements

These measurements were made in order to elucidate the nature of the decomposition products of pyridine perchromate. Solid products of reproducible analyses were obtained under isothermal or non-isothermal conditions. In either case the analyses were identical within experimental error and the mean results were: C, 28.0;

H, 2.6; N, 6.3%. These figures are extremely close to those required for the starting material, pyridine perchromate: C, 28.4; H, 2.4; N, 6.6%. It was necessary, therefore, to examine the gaseous decomposition products since an appreciable weight loss accompanied thermal decomposition.

A sample of the compound was introduced into the mass-spectrometer on a direct insertion probe and spectra recorded at temperatures between 310°K and 620°K. The major peaks were derived from oxygen, pyridine and water and, in addition, a small carbon dioxide peak could be detected. The smallness of this peak compared with that due to water suggests that a very small amount of combustion may occur and that the water peak may be due to inadequate drying of the solid. Rigorous drying was difficult to effect due to the nature of the compound. The results of our measurements ar shown in Fig. 2, in which it can be seen that the major decomposition products are oxygen and pyridine.

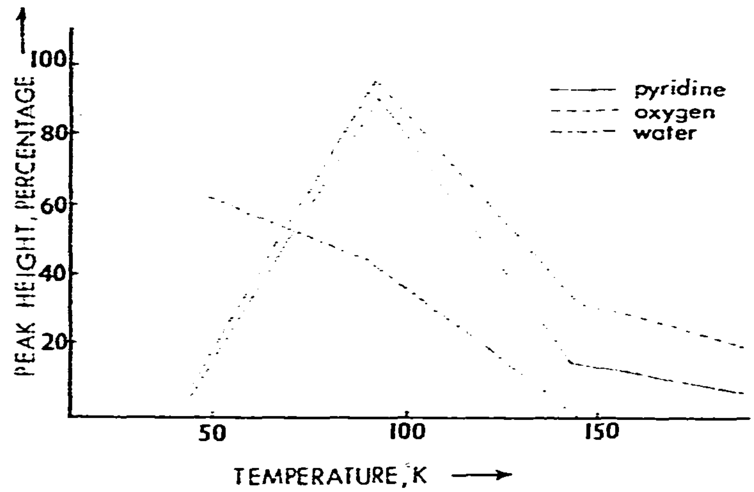

Fig. 2. Temperature dependence of parent peaks in the mass spectrum of pyridine perchromate decomposition products.

The main peaks detected in the IR spectrum of the brown decomposition product are listed in Table I, together with the peaks observed for pyridine perchromate. We also list the spectrum of pyridine-*N*-oxide. Although no evidence for the presence of this ligand was obtained from the mass spectrometric results, there are reasons to suspect the presence of at least some of this in the final decomposition product. A stoicheiometry such as $Cr_4O_{12}(py)_3$ would yield an adequate microanalysis and, in order to obtain part of the chromium as Cr^{3+} (as suggested from the EPR results) some of the oxygen must be bonded to the pyridine. Alternative formulations require the presence of diamagnetic Cr^{VI}.

The solid product which we have obtained may contain both para- and diamagnetic chromium atoms which is in agreement with the results obtained by Rai[4] from hydrolytic studies on pyridine perchromate.

TABLE I

PRINCIPAL IR BANDS (CM^{-1})[a] OF PYRIDINE-N-OXIDE, $CrO_3(py)$ AND THE DECOMPOSITION PRODUCT OF $CrO_5(py)$

Pyridine N-oxide	*$CrO_3(py)$*	*Decomposition product*
	1635 (sh)	1635 (sh)
	1610 (s)	1608 (s)
	1535 (s)	
1443 (s)	1483 (s)	1480 (s, b)
	1385 (m)	1448 (s)
	1330 (m)	
	1250 (m)	1250 (w)
1215 (s)	1195 (w)	1220 (m)
1159 (m)	1164 (w)	1158 (w)
	1057 (m)	1069 (s)
		1050 (m)
1005 (m)		1018 (m)
	940 (s)	970 (sh)
830 (s)	885 (sh)	940 (s)
763 (s)	760 (s, b)	750 (s, b)
670 (s)	675 (s)	645 (s)

[a] Intensity: s, strong; m, medium; w, weak; s, b strong and broad; sh, shoulder.

Calorimetric measurements

Rapid heating of large samples of pyridine perchromate resulted in explosive decompositions. Smaller samples (less than 5 mg) heated at 4 or 8 °K·min^{-1} decomposed smoothly and exothermally in a reproducible manner. The heat of reaction, ΔH, was -97 ± 3 kJ·mol.$^{-1}$ The reaction commenced at 335 °K, reached a maximum rate at 358 °K, and was complete by 370 °K at a heating rate of 8 °K·min^{-1}.

The kinetic results, calculated from the DSC curves were obtained by the method described in the Experimental section.

The results are shown in Table II. Although the value of n is of dubious validity in non-isothermal conditions[4-11], it is possible that a change of reaction order accompanies the larger activation energies observed at the higher values of α for a particular sample. Probably the most striking feature of the results is the very

TABLE II

KINETIC PARAMETERS OF THE DECOMPOSITION OF PYRIDINE PERCHROMATE

Sample weight (mg)	*Heating rate (°K·min^{-1})*	*Range of α*	*A*	*E (kJ·mol^{-1})*	*n*
1.95	8	0.2–0.7	4.6×10^{38}	286	0.7
2.05	8	0–0.2	1.5×10^{25}	191	0.4
2.05	8	0–0.7	2.6×10^{26}	199	0.3
2.05	8	0–1.0	1.8×10^{32}	238	0.9
2.37	4	0.4–0.9	2.8×10^{22}	165	1.1

high value of A, the pre-exponential factor. A more usual value of A is of the order of 10^{10}, which is approximately equal to the vibrational frequency initiating the decomposition[15]. High values of A have only been reported previously in a few cases and have been attributed to the presence of a diffuse interface between reactant and product[16]. The reaction which we have studied probably also proceeds via an interfacial mechanism but, in any case, we would not expect a correlation of A with any vibrational frequency of the reactant since the reaction must proceed by some type of electron-transfer mechanism (to produce Cr^{3+}) and a free-radical process can not be excluded. The long nucleation period observed in the ESR experiments is probably associated with the creation of Cr^{3+} nuclei, followed by diffusion of oxygen and pyridine and the first order ($n = 1$) growth of the nuclei. The observed and computed rates of reaction for a typical decomposition are shown in Fig. 3. The sample mass was 1.95 mg and the heating rate was $8\,^{\circ}\mathrm{K \cdot min^{-1}}$.

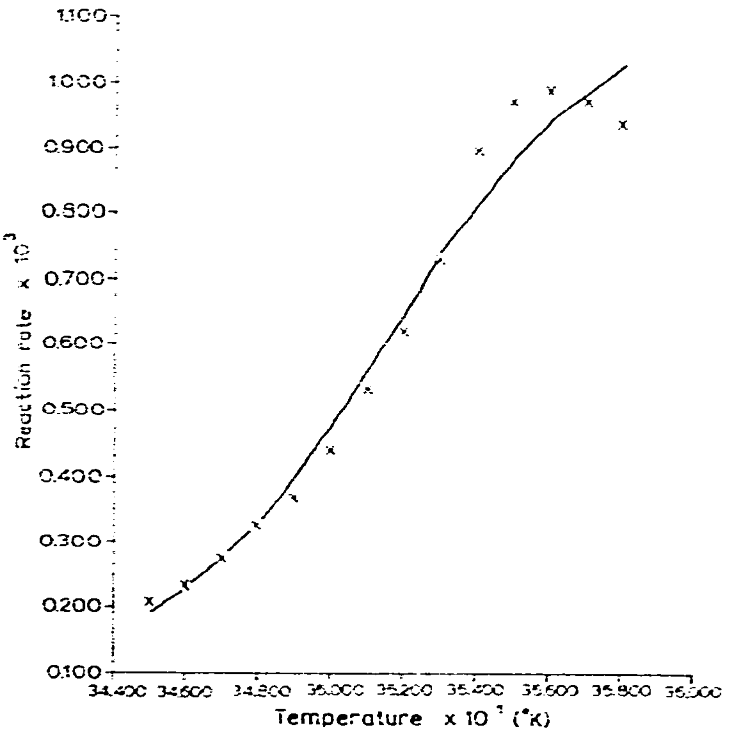

Fig. 3. Observed (×) and computed (————) rates of decomposition of pyridine perchromate.

EPR measurements

The growth of the EPR signal with time is shown in Fig. 4. The line width did not change with time so that Eqn. (1) was applicable and the ordinate in Fig. 4 is proportional to the number of paramagnetic species.

A marked induction period was observed for the room temperature decomposition (see Fig. 4) before an EPR signal could be observed. The duration of this induction period was found to depend on the initial preparation of the complex. It is probable, therefore, that the presence of small amounts of impurities may catalyse the decomposition.

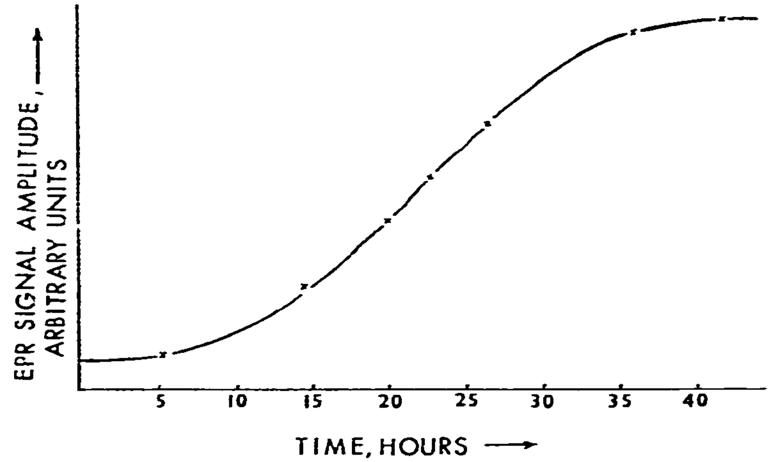

Fig. 4. Variation of the EPR signal amplitude during the isothermal decomposition of pyridine perchromate.

We calculated an approximate value of the rate constant (k) for this isothermal decomposition from a graphical solution to

$$\log\frac{d\alpha}{dt} = \log k + \log(1-\alpha)$$

where the symbols have their previous significance. The value of k was found to be 4.3×10^{-5} sec^{-1} which is considerably smaller than the calorimetric values as expected from their observed temperature dependance (Table III).

TABLE III

TEMPERATURE DEPENDENCE OF $d\alpha/dt$ AND THE RATE CONSTANT, k, FOR THE DECOMPOSITION OF PYRIDINE PERCHROMATE (1.95 mg, 8 °K·min^{-1})

Temperature (°K)	*$10^3 \times d\alpha/dt$*		*Rate constant $10^3 \times k$ (sec^{-1})*
	Observed	*Calculated*	
345	0.206	0.189	0.202
346	0.232	0.227	0.250
347	0.275	0.275	0.307
348	0.327	0.332	0.378
349	0.370	0.399	0.464
350	0.439	0.475	0.569
351	0.534	0.562	0.697
352	0.620	0.646	0.853
353	0.732	0.739	1.042
354	0.896	0.811	1.272
355	0.973	0.880	1.551
356	0.990	0.941	1.890
357	0.973	0.984	2.299
358	0.939	1.026	2.794

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