

A Raman Spectroscopic Determination of the Kinetics of Decomposition of Ammonium Chromate $(\text{NH}_4)_2\text{CrO}_4$

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Received June 27, 1988; in revised form December 12, 1988

Raman spectroscopy was used as a method in the kinetic investigation of the thermal decomposition of solid $(\text{NH}_4)_2\text{CrO}_4$. Time-dependent measurements of the intensity of the totally symmetric stretching Cr-O mode of $(\text{NH}_4)_2\text{CrO}_4$ have been made between 343 and 363 K. A short initial acceleratory period is observed at lower temperatures and the decomposition reaction decelerates after the maximum decomposition rate has been reached at all temperatures. These results can be interpreted in terms of the Avrami-Erofe'ev law $1 - (\chi_t)^{1/2} = kt$, where χ_t is the fraction of reactant at time t . At 358 K, k is equal to $1.76 \pm 0.01 \times 10^{-3} \text{ sec}^{-1}$ for microcrystals and for powdered samples. Activation energies of 97 ± 10 and $49 \pm 0.9 \text{ kJ mole}^{-1}$ have been calculated for microcrystalline and powdered samples, respectively. © 1989 Academic Press, Inc.

Introduction

Ammonium chromate $(\text{NH}_4)_2\text{CrO}_4$ decomposes to ammonium dichromate, and eventually to Cr_2O_3 , the most stable oxide of chromium at higher temperatures through a series of intermediates. The thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ to Cr_2O_3 has been extensively reported in the literature (1-7) and a few of these studies (3-5) also included the decomposition of $(\text{NH}_4)_2\text{CrO}_4$ as a precursor to the decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Il-Huyn Park (3, 4), used thermal analysis and X-ray methods to study the decomposition of $(\text{NH}_4)_2\text{CrO}_4$ while the evolved gases were also ana-

lyzed. In these studies it was confirmed that $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is formed at lower temperatures (<400 K), although under vacuum this reaction occurs at 350 K. At higher temperatures (<500 K) CrO_3 is formed, in the third step the unstable CrO_3 is decomposed (<520 K), and in the fourth step (~670 K) the CrO_2 formed from CrO_3 is reduced to Cr_2O_3 with the evolution of O_2 , CO_2 , and CO .

In another study of the kinetics of decomposition of $(\text{NH}_4)_2\text{CrO}_4$ to $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, the variation in pressure of NH_3 evolved was measured as a function of time (5). These results indicated that the decomposition obeys the contracting cylinder equation $1 - (1 - \alpha)^{1/2} = kt$ (where α is the fraction of product, k the rate constant, and

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t the time). The microscopic examination of cross section surfaces revealed that the reaction interface advances progressively inward from the crystal surfaces. Two distinct chemical steps were found to contribute to the mechanism, viz., reversible proton transfer and water elimination.

The Raman spectra of $(\text{NH}_4)_2\text{CrO}_4$ and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ are well-known (7, 8). The totally symmetric, Raman-active Cr–O stretching modes are well-separated in these two compounds and since no other bands overlap with this mode in $(\text{NH}_4)_2\text{CrO}_4$, time measurements of its intensity can be made and can accordingly be used as a method in the kinetic investigation of the thermal decomposition of this compound. However, as has already been indicated, several different decomposition reactions of $(\text{NH}_4)_2\text{CrO}_4$ can occur (3, 4) and the experimental conditions must be carefully controlled in order to ensure that CrO_3 or Cr_2O_3 decomposition products are not formed, but that $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is the only solid decomposition product.

Experimental

The Raman measurements were made on a Z-24 Dilor Raman spectrometer using a He–Ne laser to excite the spectra. A high-temperature cell, obtained from Dilor, Lille, France was used to heat the samples of analytical-grade $(\text{NH}_4)_2\text{CrO}_4$. Both powdered (ca. $0.1 \times 0.08 \times 0.04$ mm) and small microcrystals (ca. $1.0 \times 0.2 \times 0.1$ mm) of $(\text{NH}_4)_2\text{CrO}_4$ contained in open glass tubes of diameter 3 mm were used. The intensity of the $\nu_s(\text{Cr–O})$ band was recorded every 45 sec for periods up to 600 sec. The isothermal kinetic measurements were made at 343, 348, 353, 358, and 363 K, the temperatures being correct within 5 K.

The glass tubes containing the samples were not evacuated since this lowered the temperature at which $(\text{NH}_4)_2\text{CrO}_4$ decomposed to CrO_3 considerably and it was fur-

ther observed that a mixture of decomposition products was obtained upon evacuation of the samples. The samples studied were polycrystalline and in the kinetic measurements the crystal orientations did not affect the intensity of the $\nu_s(\text{Cr–O})$ band of the decomposing $(\text{NH}_4)_2\text{CrO}_4$. A polarization scrambler was also placed before the entrance slit of the spectrometer.

Rate Laws

If $\chi_{\text{CrO}_4^{2-}}$, the fraction of $(\text{NH}_4)_2\text{CrO}_4$ present at time t (as represented by the intensity of $\nu_1(A_1)$), is graphically represented against time t the shape of this plot can vary, depending on the changing geometry at the reaction interface. Different expressions can describe the reaction at different stages of the decomposition, such as the initial, accelerating, and decelerating stages. The generalized Avrami–Erofe'ev equation (10–13) can be used in these cases to interpret the data.

This equation can be written in the form

$$\ln[\ln 1/\chi_r] = n \ln t + \ln k,$$

where χ_r is the fraction of reactant present at time t , k is the rate constant, and n is the order of the reaction.

This $\ln \cdot \ln$ method of analysis can be used to determine n and consequently to obtain the kinetic expression which describes the reaction in the most satisfactory way.

Results

The Raman spectra of pure $(\text{NH}_4)_2\text{CrO}_4$ and some of its decomposition products are shown in Fig. 1 in the frequency range 800–1000 cm^{-1} . It is clearly evident in this figure that the bands at 845 cm^{-1} ($\nu_s\text{-CrO}_4^{2-}$) and at 902 cm^{-1} ($\nu_s\text{-Cr}_2\text{O}_7^{2-}$) are well-separated and it is therefore justified to assume that the intensity of the 845 cm^{-1} band in $(\text{NH}_4)_2\text{CrO}_4$ will accurately reflect the amount of $(\text{NH}_4)_2\text{CrO}_4$ in the decomposition reaction.

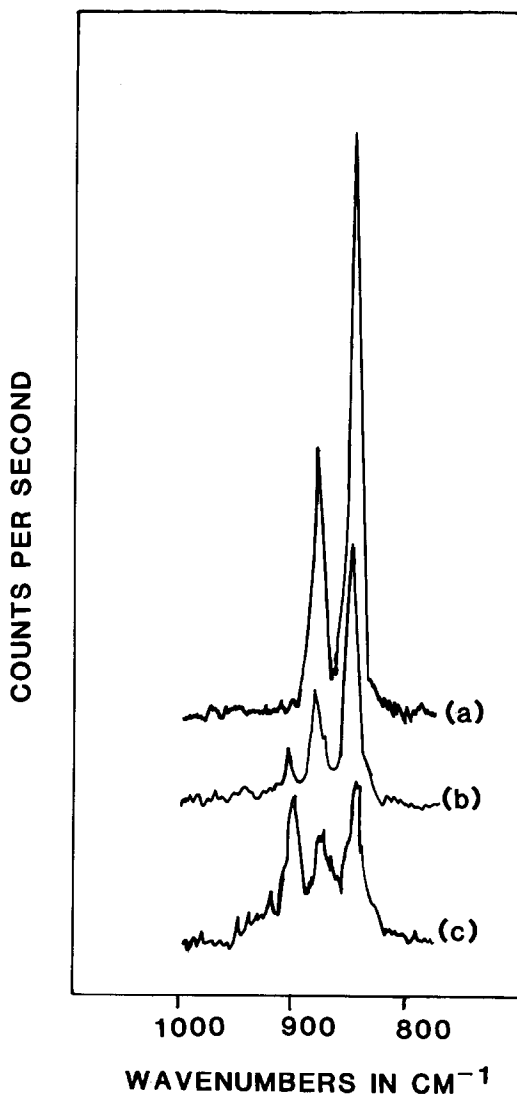


FIG. 1. The Raman spectra of $(\text{NH}_4)_2\text{CrO}_4$ in the frequency range $800\text{--}1000\text{ cm}^{-1}$. (a) The bands $\nu_1(A_1)$ at 845 cm^{-1} and $\nu_3(F_2)$ at 876 cm^{-1} of pure $(\text{NH}_4)_2\text{CrO}_4$. (b) The development of a band at 902 cm^{-1} indicates the formation of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. (c) The intensity of $\nu_2(\text{CrO})$ of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ has increased considerably while the Cr-O bands of $(\text{NH}_4)_2\text{CrO}_4$ are of much lower intensity.

The isothermal kinetic results at various temperatures have been obtained for microcrystals and powders of $(\text{NH}_4)_2\text{CrO}_4$, respectively. These results are graphically

represented in Fig. 2 for powders (with the different stages of the reactions indicated on this graph) and in Fig. 3 for microcrystals. The maximum decomposition rate is obtained sooner at higher temperatures and this point is reached during the early stages of the reaction in each case, the periods ranging from 45 to 135 sec at various temperatures after the initiation of the reaction. No induction periods were observed in the reaction; a short initial acceleratory period is observed at lower temperatures; this is however absent at 363 K . Acceleratory periods have not been detected by Rajam and Galwey (5) in the decomposition reaction of $(\text{NH}_4)_2\text{CrO}_4$, even at temperatures as low as 348 K . However, these authors used a warm-up period of a few minutes and it is possible that this could be the reason for not observing this period. The acceleratory period usually represents the growth of nuclei which are formed during an induction period. This could perhaps be accompanied by further nucleation and this period extends to the maximum rate of reaction. It is also clear from Figs. 2 and 3 that the reaction is decelerating after the maximum decomposition rate has been reached.

The $\ln \cdot \ln$ method of analysis was used to determine the kinetic expression which describes the reaction best. Accordingly, values of n were determined from $\ln[\ln(1/\chi_{\text{CrO}_4})]$ vs \ln time plots at various temperatures over intermediate ranges of the reaction. These results are summarized in Table I. Straight lines were obtained beyond $(-d\chi_{\text{CrO}_4}/dt)_{\text{max}}$. In the case of microcrystalline samples, values of n could not be accurately determined at 343 and 348 K since the $(-d\chi_{\text{CrO}_4}/dt)_{\text{max}}$ values were not sufficiently separated from the points at which the reaction can be regarded as complete. The values of n determined at 358 and 363 K for microcrystals are equal to 1.09 and 1.03 showing that the Avrami-Erofe'ev (10-13) or Mampel (14) intermediate law is followed. The values of n can, however,

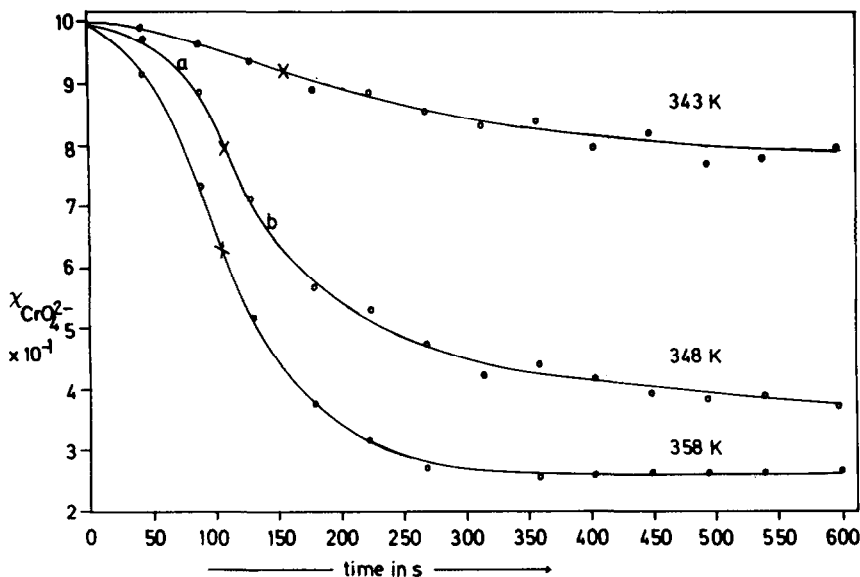


FIG. 2. The fraction of powdered $(\text{NH}_4)_2\text{CrO}_4$ ($\chi_{\text{CrO}_4^{2-}}$) graphically represented against time during decomposition at three different temperatures. The points $X(-d\chi_{\text{CrO}_4^{2-}}/dt)_{\text{max}}$ represent the points of maximum deflection at maximum rate. At 348 K the following steps are indicated, viz. (a) acceleratory period, (b) deceleratory (or decay) period, and these periods are followed by the completion of the reaction.

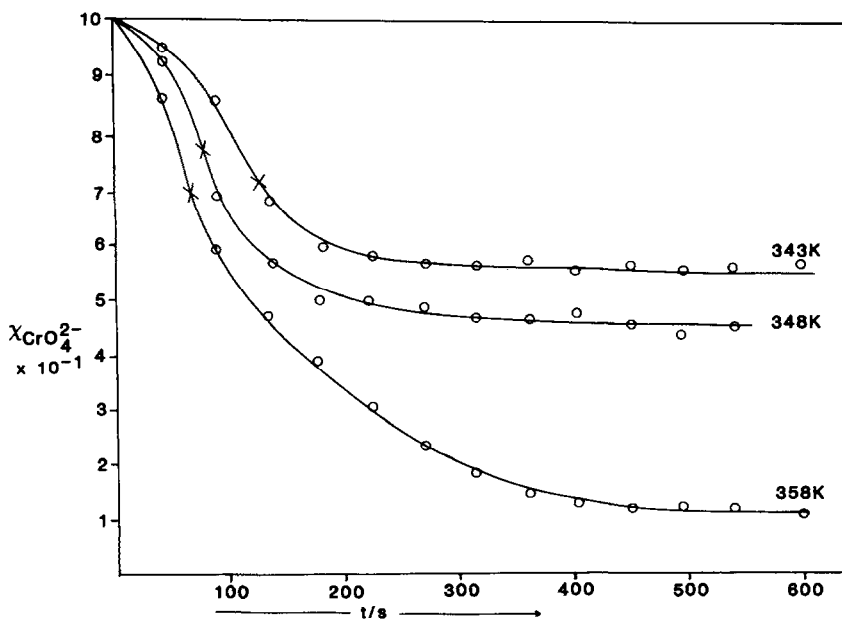


FIG. 3. The fraction of microcrystalline $(\text{NH}_4)_2\text{CrO}_4$ ($\chi_{\text{CrO}_4^{2-}}$) graphically represented against time during decomposition at three different temperatures. The points $X(-d\chi_{\text{CrO}_4^{2-}}/dt)_{\text{max}}$ represent the points of maximum deflection at maximum rate.

not be used to distinguish between the contracting volume equation, $1 - (\chi_r)^{1/3} = kt$, or the contracting cylinder equation, $1 - (a\chi_r)^{1/2} = kt$ which should give rise to values of n of 1.04 and 1.08, respectively (15). In the case of powdered $(\text{NH}_4)_2\text{CrO}_4$ the values of n vary between 0.81 and 1.10 in the temperature range concerned. These results once again indicate that the intermediate law is followed.

The obedience of some of the results to the contracting cylinder equation, $1 - (\chi_r)^{1/2} = kt$ is shown in Figs. 4 and 5. Close agreement between theory and experiment was observed at higher temperatures, particularly in the case of microcrystals. In the case of powdered $(\text{NH}_4)_2\text{CrO}_4$, a slight decrease has been observed in the rate of the reaction at later stages as is clearly evident in Fig. 4 in the case of a powdered sample at 343 K. Evidence has been provided (5) that this reduction in rate is caused by the accumulation of gaseous products. These gases are not evacuated for reasons already mentioned. The linear kinetic plots for powdered $(\text{NH}_4)_2\text{CrO}_4$ intercept the time axis at $t = 30 \pm 10$ sec. As has already been remarked there are indications of an initial acceleratory process at lower temperatures in the decomposition reaction of powdered samples. In the case of the microcrystals, the intercepts with the time axes occur at approximately $t = 0$ (Fig. 5), indicating that there is no warm-up period for the reaction here.

In Table I, values for the rate constants are given with the correlation coefficients for linear regression. Both the contracting cylinder and area equations have been used to calculate values for k at various temperatures for both microcrystals and powders. The results are virtually identical for the two and these results can therefore not be used to distinguish between these equations. However, assuming that the contracting cylinder equation is the appropriate one to represent the kinetics of this decom-

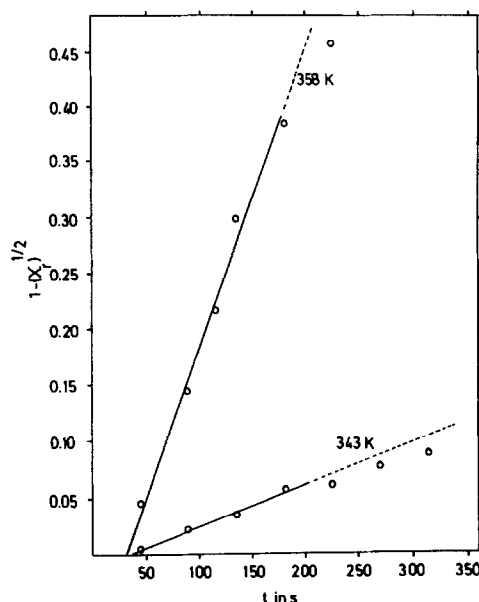
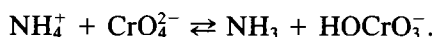


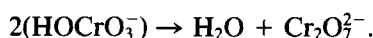
FIG. 4. The obedience of results obtained with the decomposition of powdered $(\text{NH}_4)_2\text{CrO}_4$ to the contracting cylinder equation $1 - (\chi_r)^{1/2} = kt$.

position, k varies between $4.84 \pm 0.9 \times 10^{-4} \text{ sec}^{-1}$ at 343 K and $1.76 \pm 0.01 \times 10^{-3} \text{ sec}^{-1}$ at 358 K for microcrystals and between $8.35 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$ at 343 K and $1.77 \pm 0.01 \times 10^{-3} \text{ sec}^{-1}$ at 358 K for powdered $(\text{NH}_4)_2\text{CrO}_4$. The value of k at 343 K for microcrystals is of the same order of magnitude as that of $1.33 \times 10^{-4} \text{ sec}^{-1}$ reported by Rajam and Galwey (5) for "crystallites." However, these authors showed that the reaction is influenced by sample weight and particle dimensions (the values of k being inversely proportional to the particle radius), and it could therefore be inappropriate to compare the values of k in two completely different sets of measurements.

The first step in the decomposition of $(\text{NH}_4)_2\text{CrO}_4$ is assumed to be reversible proton transfer



Water elimination then occurs



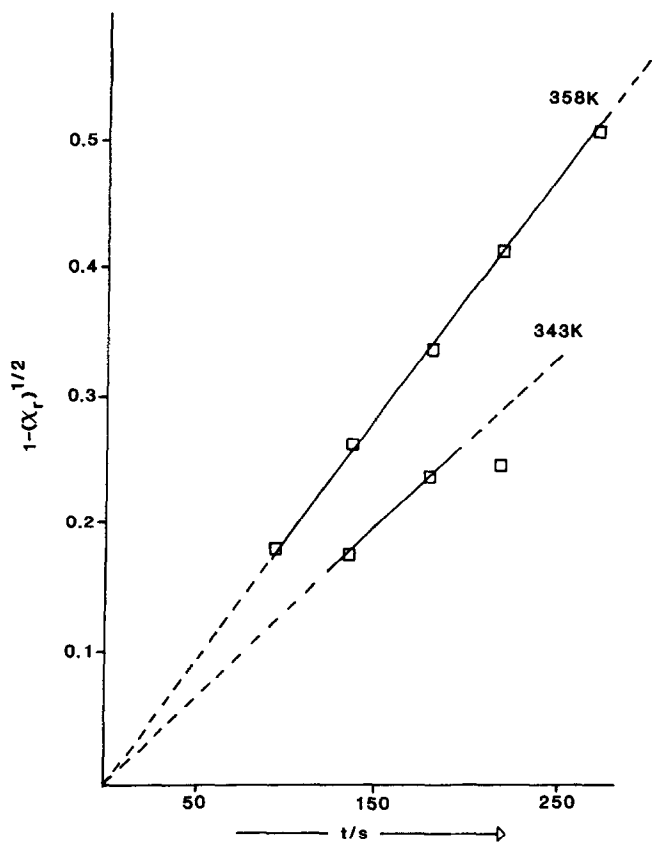


FIG. 5. The obedience of results obtained with the decomposition of microcrystalline $(\text{NH}_4)_2\text{CrO}_4$ to the contracting cylinder equation, $1 - (\chi_t)^{1/2} = kt$.

TABLE I
VALUES OF THE ORDER OF THE REACTION (n) AND THE RATE CONSTANT (k) FOR THE DECOMPOSITION REACTION OF MICROCRYSTALLINE AND POWDERED $(\text{NH}_4)_2\text{CrO}_4$

	Temperature (K)	$\ln[\ln(1/\chi_{\text{CrO}_4^{2-}}) \text{ vs } \ln t]$ (n)	$1 - (\chi_{\text{CrO}_4^{2-}})^{1/2}$		$1 - (\chi_{\text{CrO}_4^{2-}})^{1/3}$	
			$k[\text{s}^{-1}]$	r^a	$k[\text{s}^{-1}]$	r^a
Microcrystals	343	—	4.84×10^{-4}	0.814	3.53×10^{-4}	0.819
	348	—	2.69×10^{-4}	0.924	2.04×10^{-4}	0.923
	358	1.09	1.76×10^{-3}	0.995	1.36×10^{-3}	0.994
	363	1.03	1.98×10^{-3}	0.979	1.60×10^{-3}	0.979
Powder	343	0.88	8.35×10^{-5}	0.972	1.73×10^{-4}	0.970
	348	1.10	1.09×10^{-3}	0.966	7.93×10^{-4}	0.968
	353	0.81	1.28×10^{-3}	0.999	9.89×10^{-4}	0.999
	358	1.06	1.77×10^{-3}	0.999	1.37×10^{-3}	0.999

^a Correlation coefficient.

TABLE II
A COMPARISON OF THE VALUES OF LOG A, WHERE A IS THE FREQUENCY FACTOR AND E IS THE
ACTIVATION ENERGY FOR THE DECOMPOSITION OF (NH₄)₂CrO₄

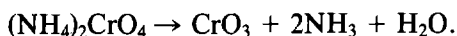
Microcrystals			Powder		
	$1 - (\chi_{\text{CrO}_4^{2-}})^{1/2}$	$1 - (\chi_{\text{CrO}_4^{2-}})^{1/3}$		$1 - (\chi_{\text{CrO}_4^{2-}})^{1/2}$	$1 - (\chi_{\text{CrO}_4^{2-}})^{1/3}$
This work			This work		
log (A/sec ⁻¹)	11.29 ± 1.45	11.8 ± 1.4	log (A/sec ⁻¹)	4.49 ± 0.9	5.4 ± 0.04
E/kJ × mole ⁻¹	97 ± 10	101 ± 12	E/kJ × mole ⁻¹	49 ± 0.9	56 ± 0.04
Galwey <i>et al.</i> (6)			Galwey <i>et al.</i> (6)		
log (A/sec ⁻¹)	10.3	—	log (A/sec ⁻¹)	6.7	—
E/kJ × mole ⁻¹	97 ± 5	—	E/kJ × mole ⁻¹	70 ± 5	—

Note. From ln *k* against 1/*T* plots.

It has been shown (5) that the proton transfer is a reversible process; however, the decomposition of (NH₄)₂CrO₄ is not reversible because of the water elimination process.

Rajam and Galwey (5) performed experiments in which the product gases were evacuated briefly and it was shown that the accumulated gases cause a reduction in the rate of the reaction, which is largely due to the effective opposition to the dissociation step due to the presence of the products.

(NH₄)₂CrO₄ can also decompose as follows:



It can be expected that if the gases are not removed by evacuation, the ammonia and water vapor will build up in the intercrystalline channels (5), thus preventing the formation of CrO₃ at lower temperatures. Upon evacuation CrO₃ is formed at lower temperatures as a decomposition product of (NH₄)₂CrO₄ (4).

The kinetics of this decomposition of (NH₄)₂CrO₄ can therefore be controlled by opposite reactions, and one must be cautious in assuming that the reaction is isokinetic at various temperatures.¹ However,

¹ We are grateful to the referee for suggesting that the kinetics of this reaction can be governed by two opposite reactions.

Rajam and Galwey (5) calculated values for the activation energy, *E*, and the preexponential factor, *A*, assuming that the Arrhenius equation $\ln k = -E/RT + \ln A$ can be applied over the temperature range 356 to 381 K. The results obtained for *E* and *A* from the graphs of ln *k* against 1/*T* in the present measurements are summarized in Table II. It is interesting to note that the values of *E* of 97 ± 10 kJ mole⁻¹ and log *A* (sec⁻¹) of 11.29 ± 1.45 closely agree with the values assigned by Rajam and Galwey (5) for this reaction. Although the rate constants *k* are almost equal at 358 K for powders and microcrystals, the activation energy for the former is almost half that of the latter, clearly demonstrating the influence of particle size on this decomposition reaction.

The close agreement which has been obtained in the decomposition reaction of (NH₄)₂CrO₄ between the values of log *A* and *E* in the Raman measurements and in the experiments in which the pressure of NH₃ evolved was measured (5), and clearly demonstrates the potential of Raman spectroscopy as a tool in the study of solid-state reactions. Generally speaking, the kinetic results can be satisfactorily interpreted in terms of either the contracting area $1 - (\chi_r)^{1/2} = kt$ or the contracting volume $1 - (\chi_r)^{1/3} = kt$ equations. Based on a micro-

scopic study (5) which was very carefully done and comprehensively reported, the former law is the appropriate one. In the present Raman measurements, the reaction could only be followed between 343 and 363 K because of instrumental limitations. The reaction is temperature-sensitive; at lower temperatures an initial acceleratory period is observed which is absent at higher temperatures.

Acknowledgments

Two of the authors (A.M.H. and D.d.W.) thank the FRD, the CSIR, and the Council of the University of Pretoria for financial support.

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