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GLOBAL DECOMPOSITION KINETICS AND CRITICAL EXPLOSION TEMPERATURES OF 2-(5-CYANOTETRAZOLATO) PENTAAMMINE COBALT (III) PERCHLORATE

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ABSTRACT

Kinetics of decomposition of 2-(5-Cyanotetrazolato) Pentaammine Cobalt (III) Perchlorate, CP, at constant pressure and constant volume were determined with isothermal and dynamic differential scanning calorimetry (DSC). The critical explosion temperature (T_c = 508K) for cylindrical CP pellets with radii of 0.238 cm was determined with accelerating rate calorimetry (ARC) operated in the isothermal mode. DSC data in the early stages of reaction at constant pressure were fitted to an autocatalytic rate law based on a second-order time dependence to obtain: $\log(k/s^{-1}) = (12.38 \pm 0.77) - (155 \pm 8)/\Theta$ where $\Theta = 2.303RT$ kJ/mol. Analysis of the ignition region at constant volume resulted in: $\log(k_i/s^{-1}) = (22.3 \pm 6.3) - (279 \pm 27)/\Theta$. Approximation of the global decomposition mechanism as a two-stage process in which all exoergicity is associated with ignition was found to yield a predicted critical temperature in good agreement with experiment.

INTRODUCTION

Decomposition of the explosive 2-(5-cyanotetrazolato) pentaammine cobalt (III) perchlorate, CP, as followed by conventional DSC at constant pressure exhibits a complex three-stage autocatalytic reactivity function. Symbolically, the global reaction mechanism may be represented as three consecutive processes:

$$CP \xrightarrow{1} A \quad \Delta H > o$$

$$A \xrightarrow{2} B \quad \Delta H < o$$

$$B \xrightarrow{3} C \quad \Delta H << o$$

where A, B, and C are the primary reaction intermediates for each stage of reaction. Stage 1 is endothermic and may occur in parallel with the exotherm of stage 2. Stage 3 is highly exothermic and corresponds to ignition. Searcy and Shanahan (ref.1) reported kinetic data for stages 2 and 3, while Pickard, Back, and Walters (ref.2) reported the kinetics for the endotherm of stage 1.

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This paper deals with the experimental measurement of the critical explosion temperature of cylindrical CP pellets and a reevaluation of the kinetics of stages 1 and 2 at both constant pressure and constant volume. By combining stages 1 and 2, the reaction mechanism may be further approximated as a two-stage process which assumes that all exoergicity is associated with the ignition process. This approach will be shown to yield a predicted critical temperature which is in accord with the experimental value determined under specific boundary conditions.

EXPERIMENTAL

DSC measurements

Isothermal and dynamic thermograms for CP decomposition were recorded with a Setaram DSC 111 interfaced to an HP-85 computer. Calibration of the calorimeter was performed electronically by the Joule effect using a 20 mW pulse and a 400s wait time. For subsequent data reduction, the calorimeter sensitivity, S, was expressed as the fourth-order polynomial,

$$\begin{aligned} S(\mu V/mW) = {} & 5.832 + 1.6149 \times 10^{-2}T - 4.286 \times 10^{-5}T^2 \\ & + 5.563 \times 10^{-8}T^3 - 3.8065 \times 10^{-11}T^4 \end{aligned} \qquad (1)$$

Peak temperatures at the maximum heat flow of the dynamic thermograms were corrected for thermal lag using the relation,

$$T = 1.64 + 0.9921(Tp) - 0.9\ (\phi) \qquad (2)$$

where Tp is the program temperature and ϕ(K/min) is the heating rate. CP was obtained from Unidynamics Corp./Phoenix, Arizona, and was used without further purification.

Isothermal measurements at constant pressure were conducted under Argon using cylindrical Aluminum crucibles crimped with a perforated lid. Since the reaction rate and explosion potential of CP are sensitive to the composition and exit rate of the product gases, the use of a perforated lid provided a convenient way of obtaining isothermal data without the danger of explosion.

Dynamic thermograms at constant volume were recorded with the aid of Setaram stainless steel security crucibles (ref.3) sealed under Argon with Nickel O-rings. All dynamic measurements were restricted to a heating rate within the range of 0.18-5K/min.

Critical explosion temperature

Time to explosion measurements were conducted with a Columbia Scientific Accelerating Rate Calorimeter (ARC). Cylindrical CP pellets possessing a nominal density of 1.5 g/cm^3 with a radius of 0.238 cm were placed in Setaram stainless steel crucibles, which in turn, were crimped with Nickel O-rings. These assemblies were loaded into wide-mouth ARC bombs (type 6) capped with pressure flanges designed for rupture at 1000 psi. With this arrangement, damage to the ARC is minimal in the event of explosion. For a typical measurement, the ARC was operated in the isothermal mode (ref.4) with a sensitivity of 0.5°C/min and an isothermal window of 150°C. Under these conditions transitions from the usual iterative heat-wait-search cycle were inhibited, and the assembly was allowed to undergo self-heating. Temperature and time were monitored continuously until the test assembly either exploded or until the CP decomposed. At temperatures below the critical temperature where neither explosion or cell rupture occurred, the time to explosion was taken as the required time for the sample self-heating to reach a maximum.

RESULTS AND DISCUSSION

Isothermal kinetics

A representative thermogram determined at 543 K as shown in Fig. 1 indicates that the decomposition of CP is complex and exhibits characteristics of autocatalysis.

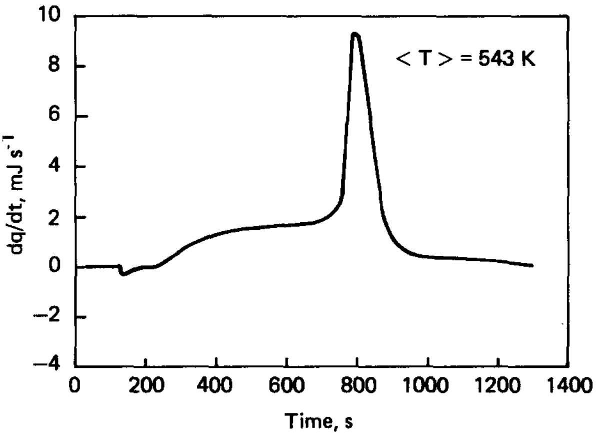

Fig. 1. Isothermal reactivity function for decomposition of CP.

The rate of CP decomposition may be expressed as:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}F(\alpha) = kF(\alpha) \qquad (3)$$

where α is the extent of reaction, A and E are the Arrhenius parameters of the rate coefficient, k, R is the ideal gas law constant, and $F(\alpha)$ is a function defined for a particular heterogeneous mechanism.

By analogy with simple homogeneous kinetics (i.e., by assuming $F(\alpha) = (1-\alpha)^n$ where n is the reaction order), Eq (3) may be rearranged in logarithmic form to obtain:

$$-\ln\left(\frac{d\alpha}{dt}\right) = n[-\ln(1-\alpha)]-\ln k \qquad (4)$$

Equation 4 indicates a linear relationship between $-\ln(d\alpha/dt)$ and $-\ln(1-\alpha)$ with slope n and intercept, $-\ln k$. A plot of Eq (4) for the thermogram given in Fig. 1 is illustrated in Fig. 2, which reveals that the reaction order ranges from -9 to 5. Fig. 2 also indicates that Eq (4) is applicable only for the decay region, for which $0.6 < \alpha < 1$.

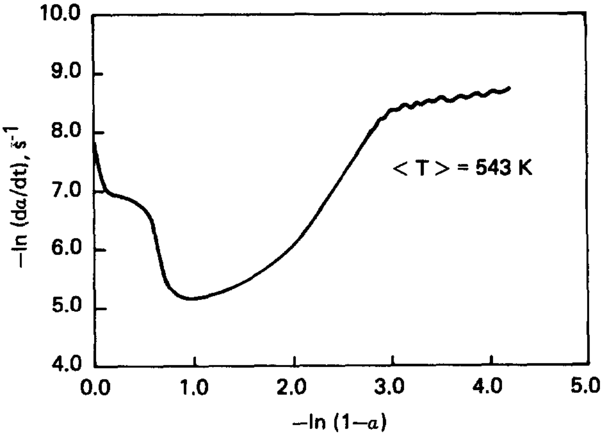

Fig. 2. Isothermal reaction order plot for decomposition of CP.

In view of the complexity of CP decomposition, Eq (3) may be expressed as the autocatalytic rate law,

$$\frac{d\alpha}{dt} = k(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \qquad (5)$$

in which n is the time dependence for the exponential growth of nuclei (ref.5). Based on previous work (ref.2), one expects the initial stage of the exothermic decomposition to be governed by a second-order time dependence; thus, Equation 5 may be expanded or rearranged (ref.5) assuming n=2 to obtain

$$\frac{d\alpha}{dt} \sim k\alpha^{0.5}(1-\alpha)^{0.774} \tag{6}$$

A global reaction plot of Eq. (6) for data determined at 543 k is given in Fig. 3 which shows that the second-order rate law is applicable for the preignition region.

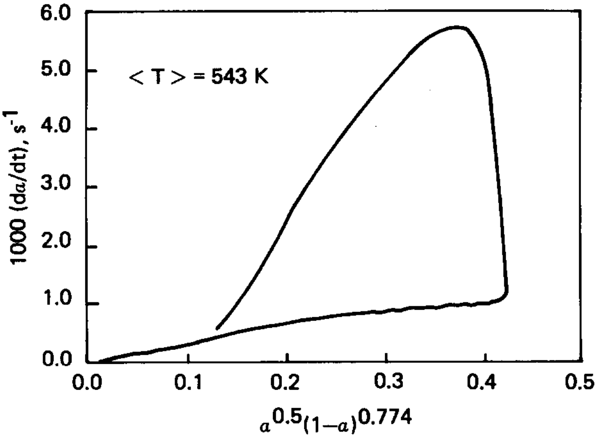

Fig. 3. Reaction rate law plot for isothermal decomposition of CP.

A summary of the kinetic data evaluated with Eq. (6) and the thermochemistry for each isothermal run is given in Table 1.

TABLE 1

Summary of isothermal kinetics and thermochemistry

Trial No.	T(k)	-ΔH(J/g)	$kx10^4(s^{-1})$[b]
1	560	2684	48.5
2	553	3056	48.9
3	550	2985	39.7
4	550	2475	36.4
5	543	2696	25.2
6	540	2817	26.1
7	540	2784	17.9
8	535	2876	15.9
9	530	2721	13.3
10	530	2449	10.1
11	526	2383	7.12
12	522	2516	5.39
13	520	3152	5.10
14	520	2771	5.90
15[a]	515	1593	2.86
		avg 2740±231	

[a] Trial 15 is deleted in calculation of average ΔH.
[b] Calculated from Eq. (6).

An Arrhenius plot for the kinetic data given in Table 1 is illustrated in Fig. 4.

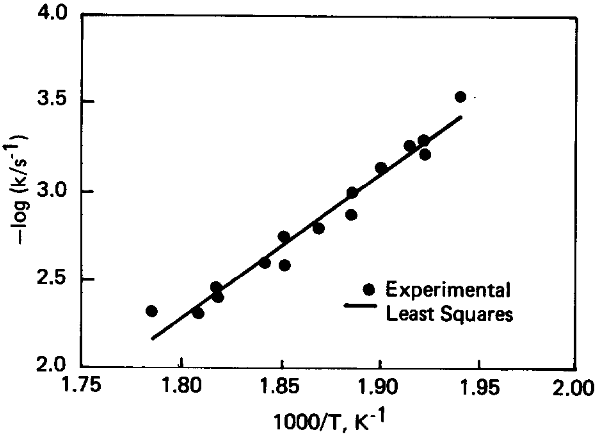

Fig. 4. Arrhenius plot for isothermal decomposition of CP.

A least squares analysis of the kinetic data for the preignition region resulted in

$$\log(k/s^{-1}) = (12.38 \pm 0.77) - \frac{(155 \pm 8)}{\Theta} \tag{7}$$

where $\Theta = 2.303RT$ kJ/mol. The error estimates represent one standard deviation. The logarithm of the observed A factor and the activation energy are in reasonable agreement with the data of Searcy and Shanahan (ref.1); namely, $\log A/s^{-1} = 13.6 \pm 0.4$ and $E = 155 \pm 7$ kJ/mol.

Dynamic kinetics

Representative dynamic thermograms determined at constant volume at heating rates of 1 and 5K/min are illustrated in Fig. 5. The dynamic thermogram determined at ϕ = 1K/min passes through a well defined maximum at T $\sim$ 588K. Dynamic measurements conducted at ϕ > 1K/min, as illustrated for ϕ = 5K/min in Fig. 5., exhibit the expected preignition reactions followed by a fast vertical rise at T $\sim$ 593K associated with CP ignition. A summary of the thermochemistry and the temperature at the maximum reaction rate for the dynamic measurements is given in Table 2.

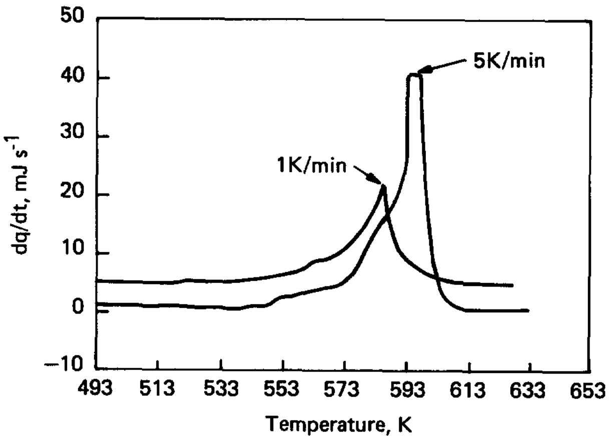

Fig. 5. Dynamic reactivity function for decomposition of CP.

TABLE 2

Summary of thermochemistry for CP decomposition at constant volume.

No.	ϕ(K/min)	Tmax(K)	-ΔE(J/g)
1	5	595.8	2358
2	5	601.5	3712
3	3	594.0	-
4	2	592.5	2884
5	1	586.2	3754
6	0.75	584.0	2387
7	0.5	574.1	2780
8	0.18	568.7	4251
			avg 3161±743

Since $F(\alpha) \sim 1$ in the initial stages of reaction, Eq. (3) implies:

$$E \sim \frac{T_2T_1}{T_2-T_1} R \ln\frac{S_2}{S_1} \quad (8)$$

where S_1 and S_2 are the heat flows at temperatures T_1 and T_2. Evaluation of the dynamic data in the initial stages of using Eq. (8) revealed that the activation energy for the preignition region at constant volume was essentially unaltered from that observed at constant pressure.

In the ignition region, recognition that d/dt (dα/dt) = 0 at the maximum rate and neglecting the smaller terms associated with F(α) in Eq. (3) results in

$$-\log\left(\frac{\phi}{T^2}\right) \sim \frac{E}{2.303R}\left(\frac{1}{T}\right) + \log\frac{RA}{E} \tag{9}$$

A rate plot according to Eq. (9) for the dynamic data summarized in Table 2 is given in Fig. 6.

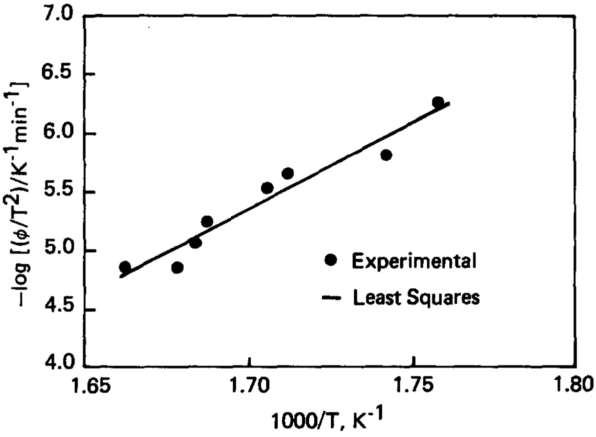

Fig. 6. Rate plot for dynamic decomposition of CP at constant volume.

Least squares analysis of the dynamic data in the ignition region at constant volume resulted in:

$$\log(k_i/s^{-1}) = (22.3\pm6.3) - \frac{(279\pm27)}{\theta} \tag{10}$$

The logarithm of the observed A factor and the activation energy at constant volume in the ignition region are considerably larger than the results, $\log(A/s^{-1}) = 19.7 \pm 0.7$ and $E = 205 \pm 7$, reported by Searcy and Shanahan (ref.1) at constant pressure. The higher activation energy at constant volume is not unexpected, since it is well established that production of NH_3 in the preignition stage inhibits the growth of the ignition reaction (ref.2).

Critical explosion temperature

The observed time to explosion plot and the measured critical temperature, T_c = 508K, determined for cylindrical CP pellets are illustrated in Fig. 7.

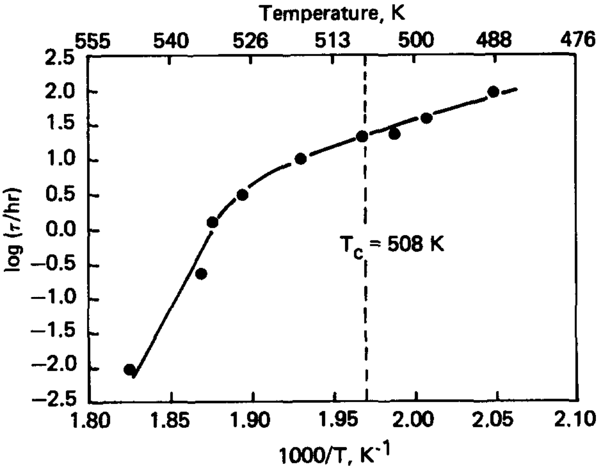

Fig. 7. Observed time to explosion curve for cylindrical CP pellets.

The plot of Fig. 5 reveals a marked curvature at $T > T_c$ associated with the change in apparent activation energy that occurs as the exotherm grows to ignition.

The preignition stages 1 and 2 of CP decomposition may be combined so that the global mechanism may be further approximated as:

$$CP \xrightarrow{1'} B$$

$$B \xrightarrow{3} C + Q$$

where it is assumed that all exothermicity, Q, is associated with the ignition process. This implies that the critical condition is

$$\frac{d \ln k_1'}{dT} > \frac{1}{T_c - T_o} \qquad (11)$$

where T_0 is ambient temperature, or that the critical temperature is determined solely by the kinetics for reaction 1' (ref.6,7). Under Semenov boundary conditions, the critical condition for an autocatalytic reaction (ref.7) is given by

$$\frac{E}{RT_c^{\,2}}\, QAe^{-E/RT_c} = \frac{hS}{\rho V F(\alpha_m)} \tag{12}$$

where h and S are the apparent heat-transfer coefficient and surface area of the vessel, ρ is density, V is volume, and $F(\alpha_m)$ is the maximum of the autocatalytic kinetic function. By choosing $H = Ve\delta\lambda/Sr^2$ (ref.7) where δ is the critical parameter for the Frank-Kamenetskii relation (δ = 3.32, 2.0, and 0.88 for spheres, cylinders, and slabs), r is the charge radius, and λ is the thermal conductivity, Eq. (12) may be rearranged to obtain

$$T_c = \frac{E}{R\,\ln\left[\dfrac{\rho r^2 QAEF(\alpha_m)}{R\lambda\delta T_c^{\,2}}\right]} \tag{13}$$

Equation (13) is equivalent to the Frank-Kamenetskii equation (ref.6) if $F(\alpha_m)$ is approximated as unity.

Differentiation of Eq. (5) yields $\alpha_m = 1\text{-}e^{-1+1/n}$ which gives $F(\alpha_m) = (2e)^{-\frac{1}{2}}$ for n = 2. With this result, Eq. (13) may be solved by interation using $\lambda = (10.9 \pm 2) \times 10^{-4}$ J/(cm°Cs) (ref.8), ρ = 1.5 g/cm^3, r = 0.238 cm, and δ = 2 along with Q = 2740 ± 231 J/g, $\log(A/s^{-1})$ = 12.38 ± 0.77, and E = 155 ± 8 kJ/mol determined at constant pressure. This approach gives T_c = 509K which is in good agreement with the experimental result, T_c = 508K.

Use of the Frank-Kamenetskii relation (ref.6) obtained from Eq. (13) by assuming $F(\alpha_m) = 1$ leads to the lower result, T_c = 498K. As demonstrated by Rogers (ref.9), the Frank-Kamenetskii equation has proved invaluable for prediction of the critical temperatures of organic explosives. However, for the explosive CP it appears that explicit accounting for autocatylsis is necessary in order to obtain reasonable predictions for the critical temperature. Agreement between theory and experiment suggests that Eq. (13) may be used for predicting the critical temperature for other geometries of arbitrary size. A plot of critical temperature versus charge radius calculated from Eq. (13) for cylinders, spheres, and slabs is given in Fig. 8.

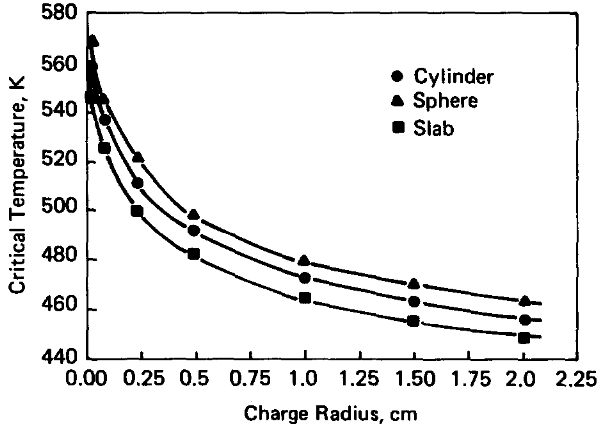

Fig. 8. Variation of CP critical temperature with charge radius.

Figure 8 indicates that the potential for thermal explosion at constant radius in the lower temperature regime varies in the order, sphere < cylinder < slab. This trend is qualitatively consistent with the expectation that the critical temperatures increase with surface-to-volume ratios, which are 3/r, 2/r, and 1/r, respectively for spheres, cylinders, and slabs (ref.10). It is anticipated that the model presented here may be useful for the prediction of critical temperatures of CP under different conditions of heat transfer.

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