

DSC AND TG STUDY OF THE STABILITY IN VACUUM OF FERROCENYL COMPOUNDS AND THEIR COMPATIBILITY WITH AMMONIUM PERCHLORATE

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ABSTRACT

Ferrocenyl compounds are used as burning rate modifiers for propellants containing ammonium perchlorate. An admixture of a ferrocenyl compound and ammonium perchlorate is highly sensitive to an electrostatic discharge. When ammonium perchlorate is added to a propellant mix, a cloud of ammonium perchlorate dust is formed above the mix, and if the ferrocenyl compound is volatile at the mixing temperature of 150°F and at 5 mm vacuum then a potentially hazardous operation may exist. A simple, fast, isothermal and dynamic thermogravimetry method was developed to determine the stability and half-life of the ferrocenyl compound under processing conditions. The half-lives of nine ferrocenyl compounds were found to range from one hour to over one year in vacuo at 150°F. Dynamic DSC showed interactions between the components in the mixture. In a vacuum, individual ferrocenyl compounds and ammonium perchlorate showed endothermic peaks due to decomposition and sublimation, respectively. In the mixture exothermic decomposition peaks were observed for the moieties at lower temperatures than those for the neat components. The activation energies for the thermal decomposition of the ferrocenyl compounds were decreased by 20% in the mixtures.

INTRODUCTION

Ferrocenyl derivative compounds have been found to increase the burning rate and to have low pressure exponents in ammonium perchlorate (AP) based propellants. However, some of the problems [1–3] encountered with these catalysts were volatility, migration, oxidation stability, impurities, and degradation in the presence of air and AP with resultant short pot-life in isocyanate cured propellants. Attempts [4–6] have been made to synthesize ferrocene derivatives which are non-volatile or which may bond to either the binder or AP and thereby eliminate migration and improve resistance to oxidation.

It is known that a mixture of a ferrocenyl compound and AP is highly sensitive to an electrostatic discharge. When AP is added to a propellant mix, a cloud of dust is formed above the mix and if the ferrocenyl compound

is volatile at the mixing temperature of 150°F and 5 mm vacuum then a potentially hazardous operation may exist. Accordingly a simple, fast, method to determine the volatility of ferrocenyl compounds under processing conditions was needed. Isothermal thermogravimetry (TG) filled this requirement. Later experience showed that a dynamic TG method, which is faster than isothermal TG, could also be used to indicate volatility. Thus, TG may be used as a screening technique for ferrocenyl compounds, and only those compounds which have low volatility would be incorporated into a propellant and thereby increase the safety of the mixing operation.

The interactions between ferrocenyl compounds and AP when they are mixed together may be followed more conveniently by dynamic DSC than TG. The endothermic thermal decomposition peaks of the ferrocenyl compounds and the endothermic sublimation peak for AP became exothermic peaks in the mixtures and shifted to lower temperatures.

EXPERIMENTAL

Instrumentation

DuPont 1090 and 990 thermal analyzers were used with a 951 TG module and a pressure DSC cell for vacuum operations. Dynamic TG and DSC runs were carried out at heating rates of 0.5 to 20°C min⁻¹ in a vacuum of 5 mm and at 10°C min⁻¹ in nitrogen or air. Isothermal TG runs were always in a vacuum; the furnace was at the desired temperature before the sample was placed in the furnace. For DSC runs the sample was in a sealed pan with a pin-hole in the cover.

Sample

The nine ferrocenyl compounds studied are listed in Table 1. HYCAT-6 and Catocene were liquids and were obtained commercially, the rest were solids and synthesized in our laboratory [4]. Sample mass was 7 ± 2 mg for TG and 3 ± 1 mg for DSC. The admixtures were prepared by mixing the ingredients together without grinding in a 1:1 ratio by weight and taking aliquots for the thermal runs.

Kinetic methods

The kinetic data generated by isothermal TG were analyzed by three methods. They are as follows: (1) the Manche-Carroll [7] method where $\log(\Delta\alpha/\Delta t/\Delta(1/T))$ is plotted to obtain $E/2.3R$, α is the fraction volatilized and $\Delta\alpha/\Delta t$ is the rate at fixed values of α . The Arrhenius frequency factor is obtained from the equation $\log A = E/2.3RT + \log(\Delta\alpha/\Delta t)$; (2) a

TABLE 1

Isothermal TG kinetic data for volatilization in vacuum of ferrocenyl compounds

Compound	E^a	$\log A^b$	$\tau_{0.5}^c$
Ferrocene aldehyde dimethylhydrazone	25.5	14.44	1 h
Ferrocenyl(dimethylaminoethyl)ketone	34.2	19.70	2.5 h
1-Ferrocenoyl-4-methyl piperazine	28.1	12.92	2.5 m
4,4-Diferrocenylpentanoic acid	35.7	15.32	1 y
1,4-Diferrocenoyl piperazine	32.4	12.23	1 y
1-(<i>N</i> -Ferrocenoyl-2-aminoethyl)-4-ferrocenoyl piperazine	37.0	14.18	1 y
bis(2-Ferrocenylethyl)disulfide	31.8	13.26	1 y
Hycat-6	27.9	12.38	0.5 y
Catocene	24.3	10.49	2.5 m

^a E is the activation energy (kcal mol⁻¹).^b $\log A$ is the Arrhenius frequency factor (min⁻¹).^c $\tau_{0.5}$ is the half-life for a first order reaction at 150°F and a vacuum of 5 mm. h, hour; m, month; y, year.

plot of $\log(1 - \alpha)$ vs. time to obtain the rate constant ($k/2.3$) followed by a plot of $\Delta \log k/\Delta(1/T)$ to obtain $E/2.3R$; the frequency factor is given by $\log A = \log k + E/2.3RT$ and (3) the Kishore [8] method where $\Delta \log t_{0.5}/\Delta(1/T)$ is plotted to obtain $E/2.3R$, $t_{0.5}$ is the time when the fraction volatilized, $\alpha = 0.5$. Dynamic TG data were analyzed according to the method of Flynn and Wall [9] and Ozawa [10]. The basic equation is $\Delta \log \beta/\Delta(1/T) \approx 0.457 E/R$ where β is the programmed heating rate and T is the temperature at a constant degree of conversion. The Arrhenius frequency factor may be calculated from the equation

$$\log A = 0.457 E/RT + 2.315 + \log \beta - \log E/R + \log F(C) \quad (1)$$

where $F(C)$ is a function of the degree of conversion and Rogers and Smith's equation [11]

$$\log A = \log \beta + \log E/RT_{\max}^2 + 0.435 E/RT_{\max} \quad (2)$$

where T_{\max} is the reaction peak maximum which in the TG curve is the maximum of the derivative peak. The dynamic DSC data were analyzed in the same manner as the dynamic TG data, however T in the equation is now the peak temperature.

DISCUSSION

TG Studies

The dynamic TG curves of the nine ferrocenyl compounds investigated are shown in Figs. 1–9. The thermal stability decreases or the rate of

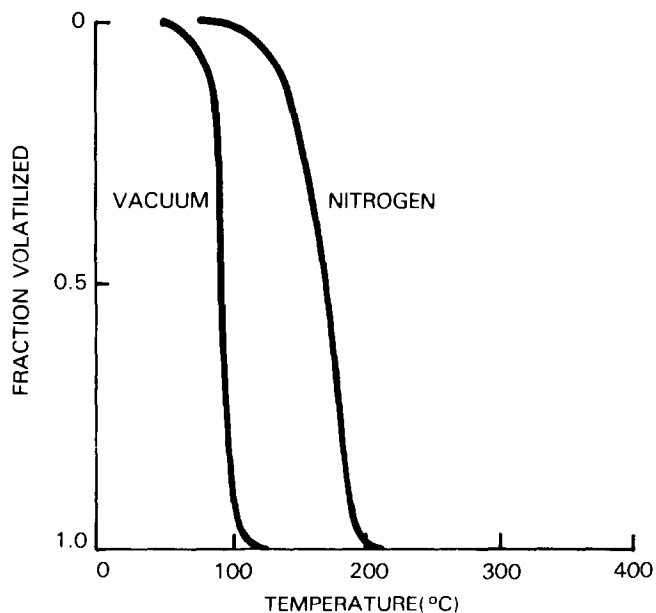


Fig. 1. TG curves in vacuum and nitrogen at $10^{\circ}\text{C min}^{-1}$ for volatilization of ferrocene aldehyde dimethyl hydrazone.

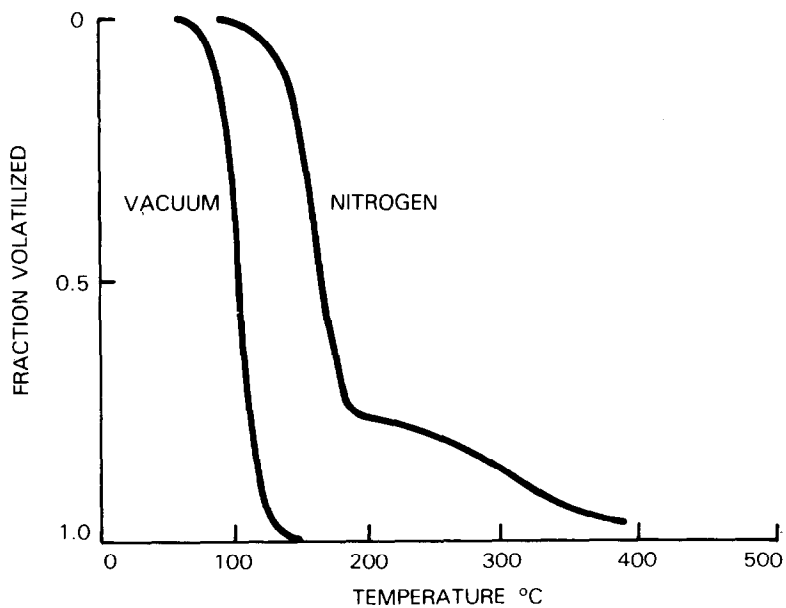


Fig. 2. TG curves in vacuum and nitrogen at $10^{\circ}\text{C min}^{-1}$ for volatilization of ferrocenyl dimethylaminoethyl ketone.

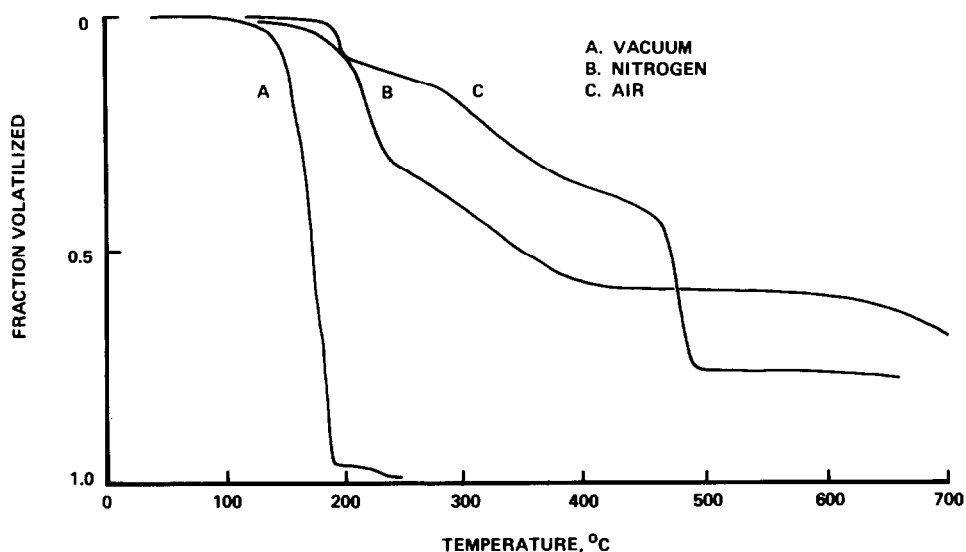


Fig. 3. TG curves for volatilization of 1-ferrocenyl-4-methyl piperazine at $10^{\circ}\text{C min}^{-1}$.

volatilization increases as the sample atmosphere changes from air to nitrogen to vacuum. The fraction volatilized in vacuum shows only a single step while in nitrogen or air there may be two or more steps in the TG curve which indicates that a more complex reaction is taking place.

Typical isothermal volatilization curves are shown in Fig. 10. The log of the slopes ($\Delta\alpha/\Delta t$) of these plots vs. the reciprocal of the absolute temperature (Fig. 11) yield activation energies (Table 1). The isothermal curves may be analyzed also in the form $\log(1 - \alpha)/\Delta t$ vs. temperature in Figs. 12 and

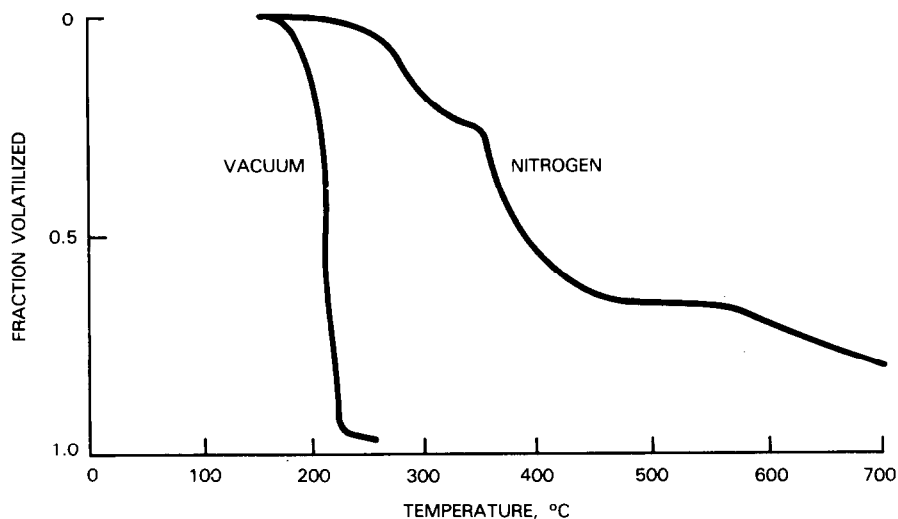


Fig. 4. TG curves in vacuum and nitrogen at $10^{\circ}\text{C min}^{-1}$ for volatilization of 4,4-diferrocenyl pentanoic acid.

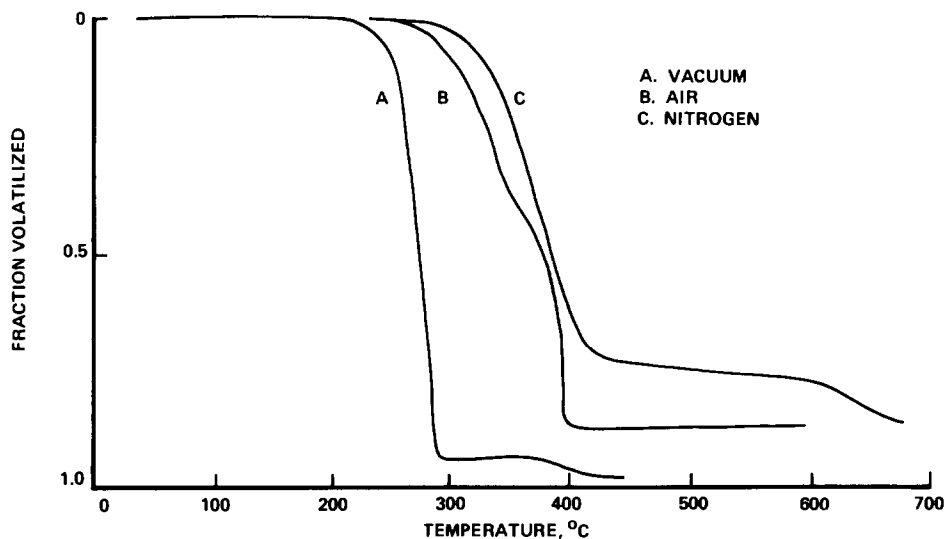


Fig. 5. TG curves for volatilization of 1,4-diferrocenoyl piperazine at $10^{\circ}\text{C min}^{-1}$.

13 assuming a first order reaction to obtain activation energies. Another common isothermal method to obtain kinetic data is to plot the log of the time it takes for the sample to volatilize to half its original value vs. the reciprocal of the absolute temperature (Fig. 14). A reduced time plot, i.e., $t_R = t/t_{0.5}$ where $t_{0.5}$ is the time when the fraction volatilized, $\alpha = 0.5$, is

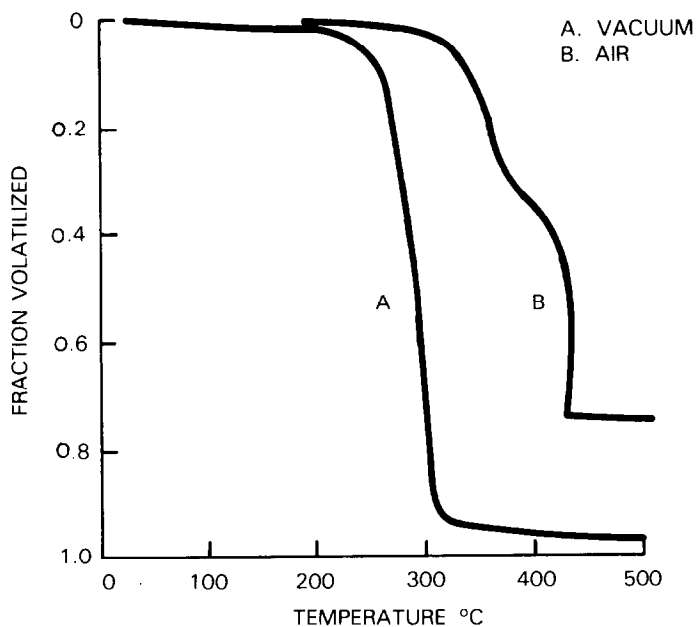


Fig. 6. TG curves for volatilization of 1-(*N*-ferrocenoyl-2-aminoethyl)-4-ferrocenoyl piperazine at $10^{\circ}\text{C min}^{-1}$.

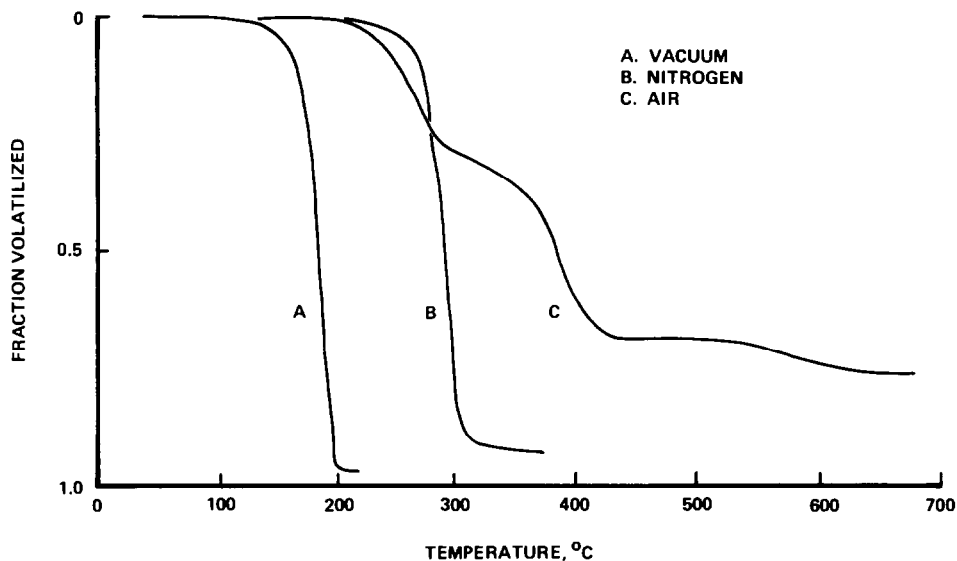


Fig. 7. TG curves for volatilization of bis(2-ferrocenylethyl) disulfide at $10^{\circ}\text{C min}^{-1}$.

shown in Fig. 15. The utility of this plot is that if the TG curves at various isothermal temperatures superimpose under an α vs. t_R plot then the order of the reaction at different temperatures is constant, i.e., the kinetic behavior remains the same. Figure 15 shows a straight-line plot.

Kinetic data may be obtained from dynamic TG curves by a variable heating rate plot. Figure 16 shows a dynamic plot (log heating rate) and an

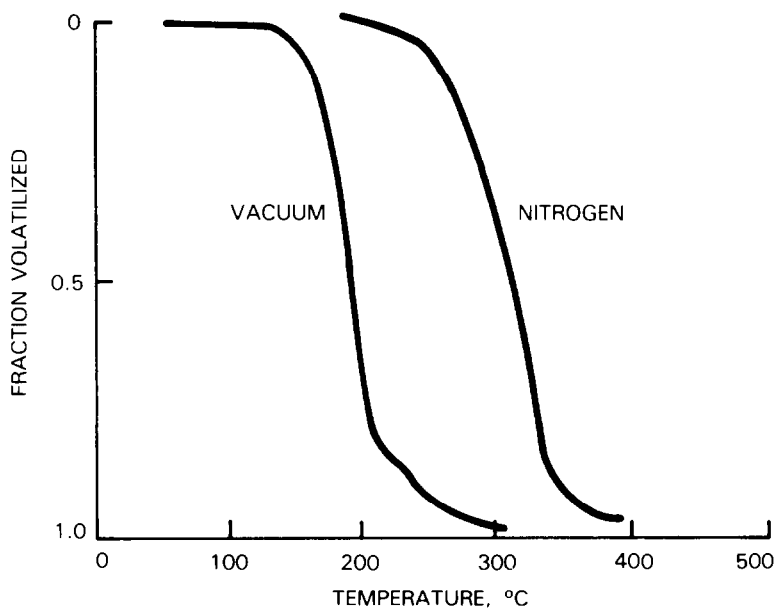


Fig. 8. TG curves in vacuum and nitrogen at $10^{\circ}\text{C min}^{-1}$ for volatilization of Hycat-6.

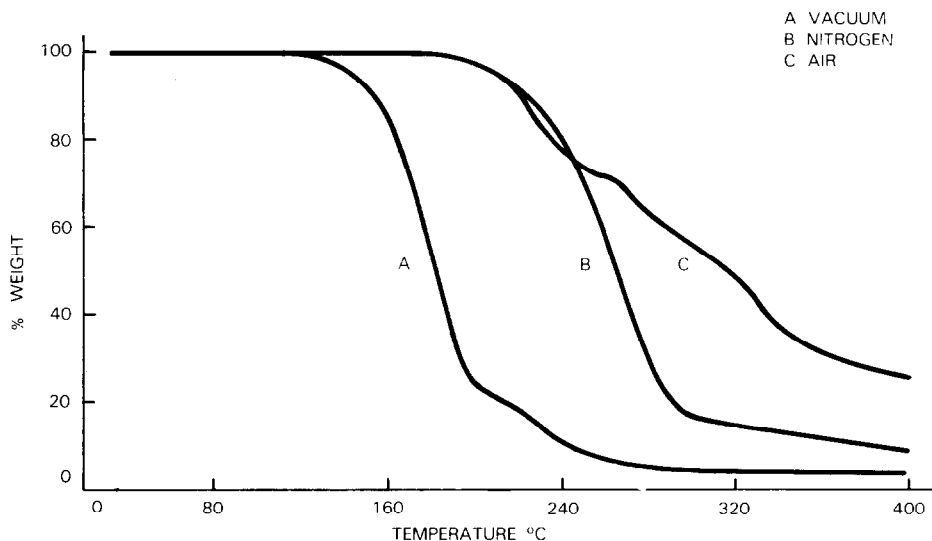


Fig. 9. TG curves for volatilization of Catocene at $10^{\circ}\text{C min}^{-1}$.

isothermal plot ($\log \Delta\alpha/\Delta t$) vs. the reciprocal of the absolute temperature for the volatilization of Catocene; the agreement between the kinetic constants is very good. In the present study, agreement between the activation energies obtained by the methods of Manche-Carroll and Flynn-Wall, and Ozawa is about $\pm 1 \text{ kcal mol}^{-1}$, while between Manche-Carroll and Kishore, and first order plots is about $\pm 2.5 \text{ kcal mol}^{-1}$.

The activation energies and frequency factors reported in Table 1 were obtained by the method of Manche-Carroll using $\log \Delta\alpha/\Delta t$ plots. Table 1

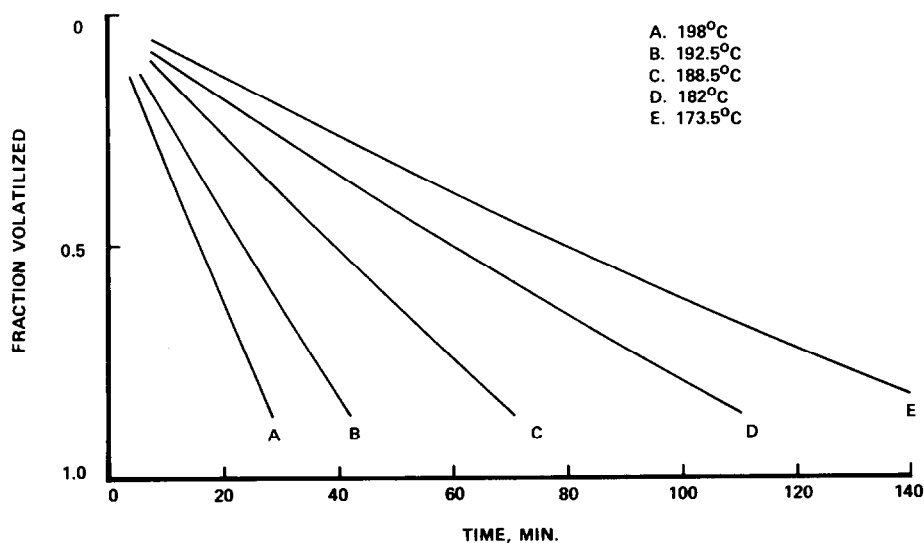


Fig. 10. Isothermal volatilization in vacuum of bis(2-ferrocenylethyl) disulfide.

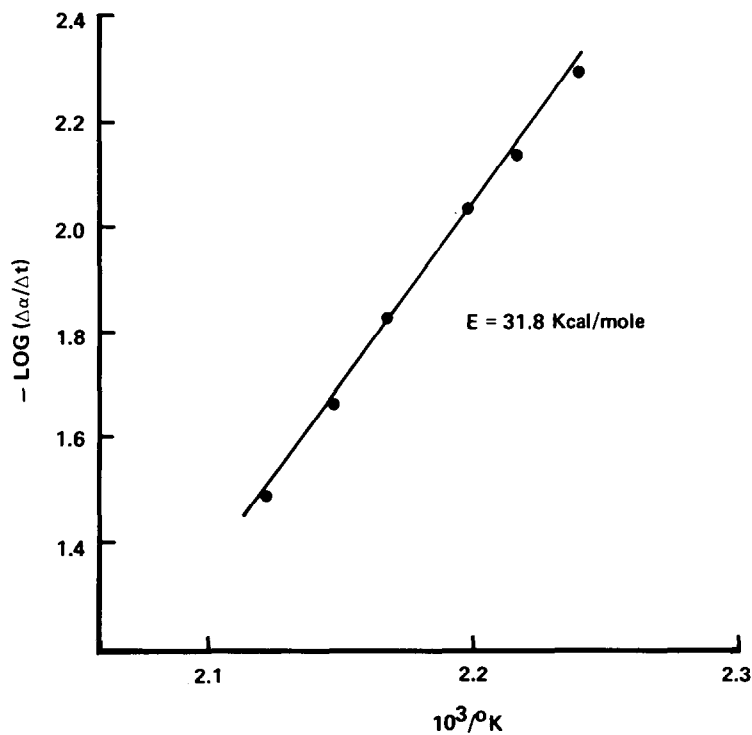


Fig. 11. Plot of $\log(\Delta\alpha/\Delta t)$ vs. reciprocal of absolute temperature for volatilization in vacuum of bis(2-ferrocenylethyl) disulfide.

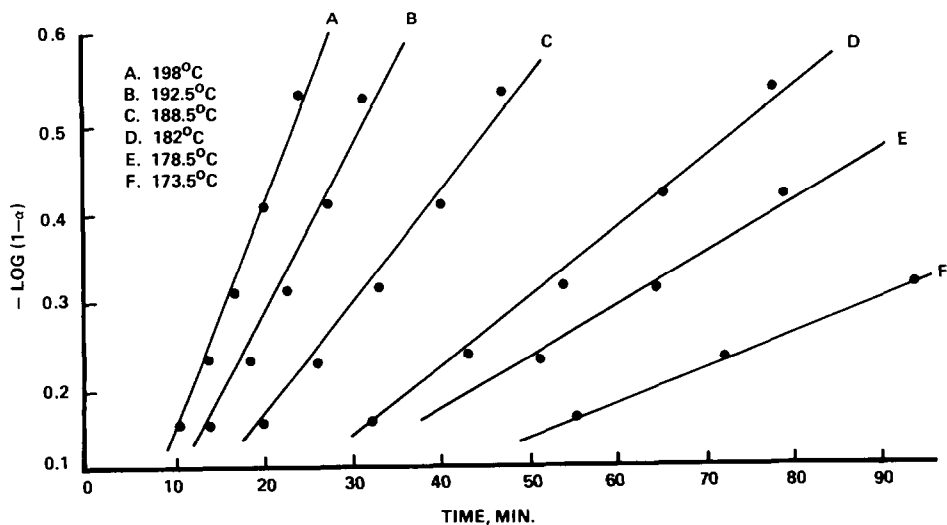


Fig. 12. First order plot for volatilization in vacuum at various temperatures for bis(2-ferrocenylethyl) disulfide.

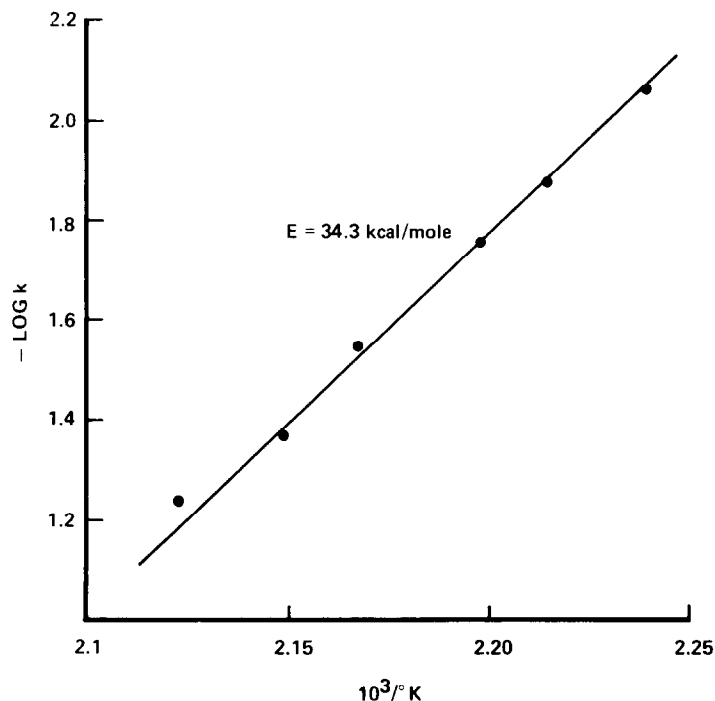


Fig. 13. Arrhenius plot for volatilization in vacuum of bis(2-ferrocenylethyl) disulfide.

also includes values for the half-life of the volatilization reaction at 150°F and 5 mm vacuum assuming a first order reaction, $t_{1/2} = 0.693 k^{-1}$. The half-life is the time required for the concentration of a sample to decrease to one-half of its value. The half-life data in Table 1 indicate that only two ferrocenyl compounds, namely ferrocene aldehyde dimethylhydrazone and ferrocenyl (dimethylaminoethyl) ketone, are sufficiently volatile in a vacuum at 150°F that they could present a safety problem in the mixing operation with AP based propellants.

Inspection of the half-life volatilization data in Table 1 obtained from isothermal TG and the dynamic TG curves in vacuum shown in Figs. 1–9 resulted in the selection of the dynamic TG curves shown in Fig. 17; it is readily apparent that ferrocenyl compounds which have a fraction volatilization of $\alpha = 0.5$ around 100°C have short half-lives (hours) and therefore would automatically be excluded from incorporation into AP based propellants. Compounds whose temperatures were above 150°C at $\alpha = 0.5$ would have long half-lives (weeks) and therefore would be a candidate for further study as a burning rate modifier.

DCS Studies

Figure 18 shows dynamic DSC curves for AP; in nitrogen or air an

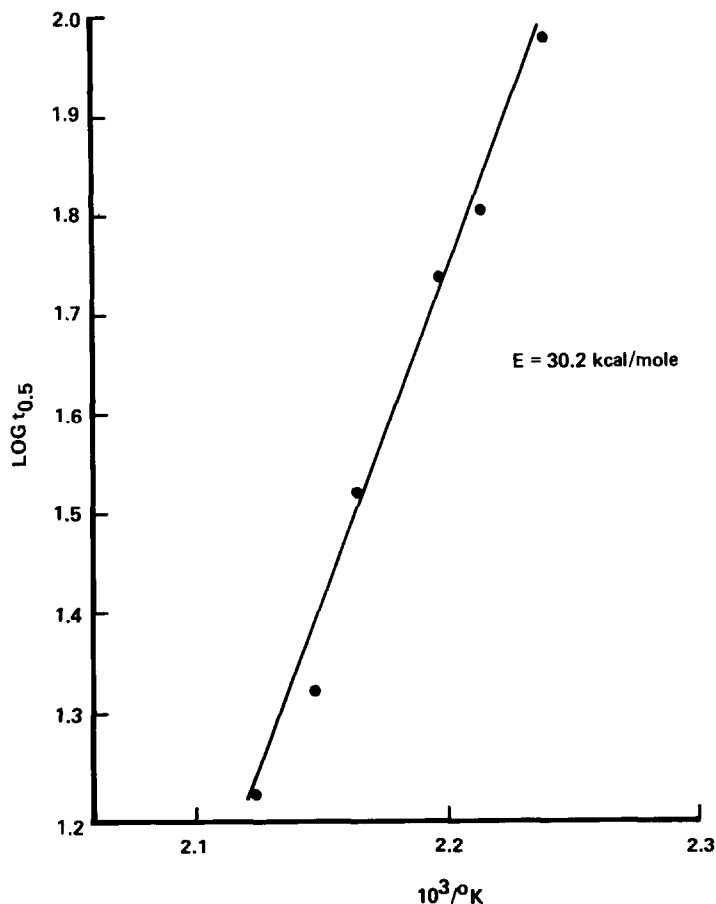


Fig. 14. Plot of $\log t_{0.5}$ vs. reciprocal of absolute temperature for volatilization in vacuum of bis(2-ferrocenylethyl) disulfide.

endothermic phase transition and low and high temperature exothermic decomposition peaks are observed using a sealed pan with a pin-hole in the cover while in a sealed pan only one exothermic decomposition peak was found. In vacuum a single endothermic peak is observed in this temperature region which is due to the sublimation of AP; an activation energy of $21.2 \text{ kcal mol}^{-1}$ and $\log A$ of 7.57 min^{-1} was calculated for the sublimation process using a DSC variable heating rate method. A TG variable heating rate method for the sublimation of AP in vacuum gave an activation energy of $22.0 \text{ kcal mol}^{-1}$ and $\log A$ of 8.53 min^{-1} . Agreement between the dynamic DSC and TG methods was very good for the kinetic constants. The temperature range investigated was 270 to 380°C for DSC and 220 to 300°C for the TG derivative peaks. Jacobs and Whitehead [12] in their review article on AP mentioned that an activation energy of $25.4 \text{ kcal mol}^{-1}$ was found for the effect of temperature on the electrical conductivity of AP

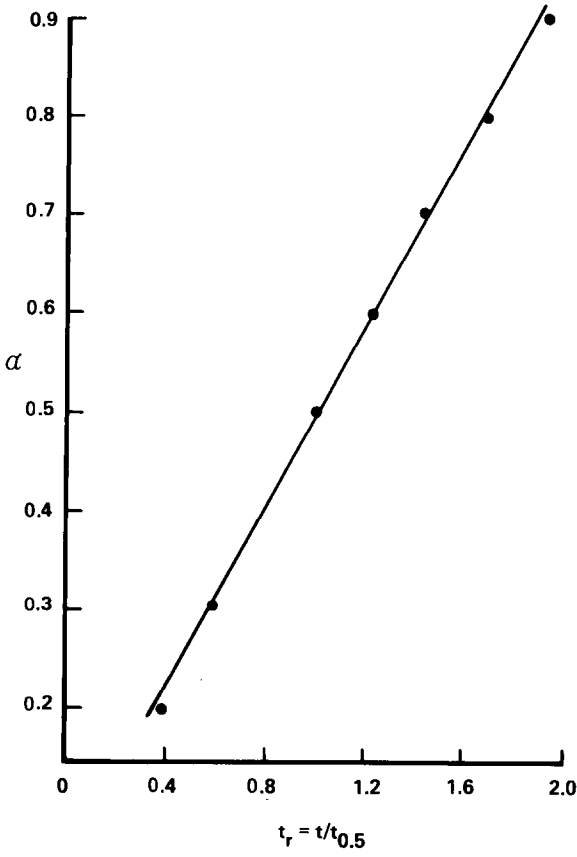


Fig. 15. Reduced time plot for volatilization in vacuum of bis(2-ferrocenylethyl) disulfide

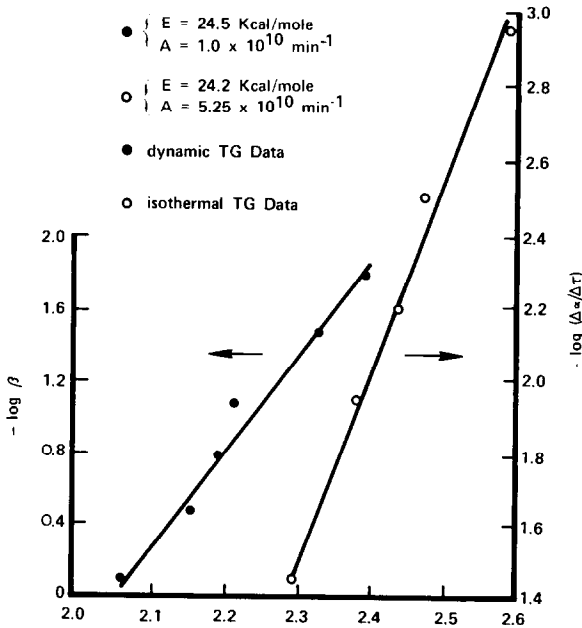


Fig. 16. Arrhenius plots for volatilization of Catocene in vacuum.

- A. Ferrocene aldehyde dimethyl hydrazone, $\tau_{0.5} = 1$ hr.
 B. 1 - Ferrocenyl -4-methyl piperazine, $\tau_{0.5} = 2.5$ mo.
 C. Hycat -6, $\tau_{0.5} = 0.5$ yr.
 D. 1,4-Diferrocenyl piperazine, $\tau_{0.5} > 1$ yr.

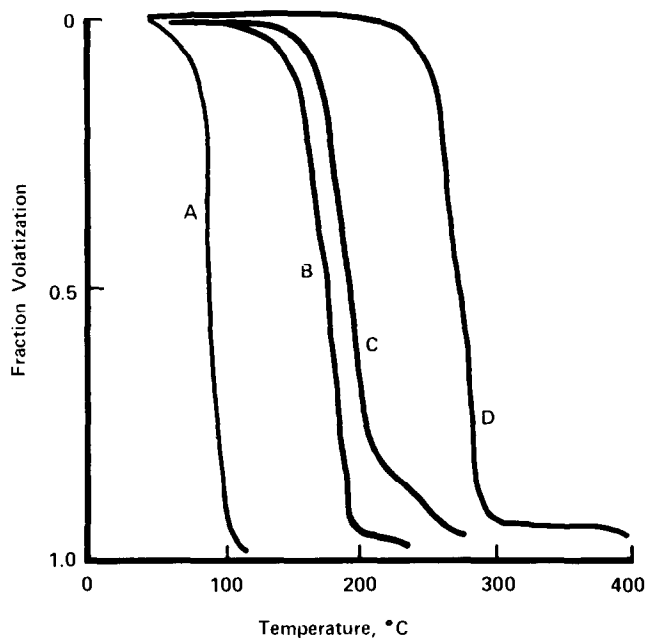


Fig. 17. Dynamic TG in vacuum at $10^{\circ}\text{C min}^{-1}$ for ferrocene compounds.

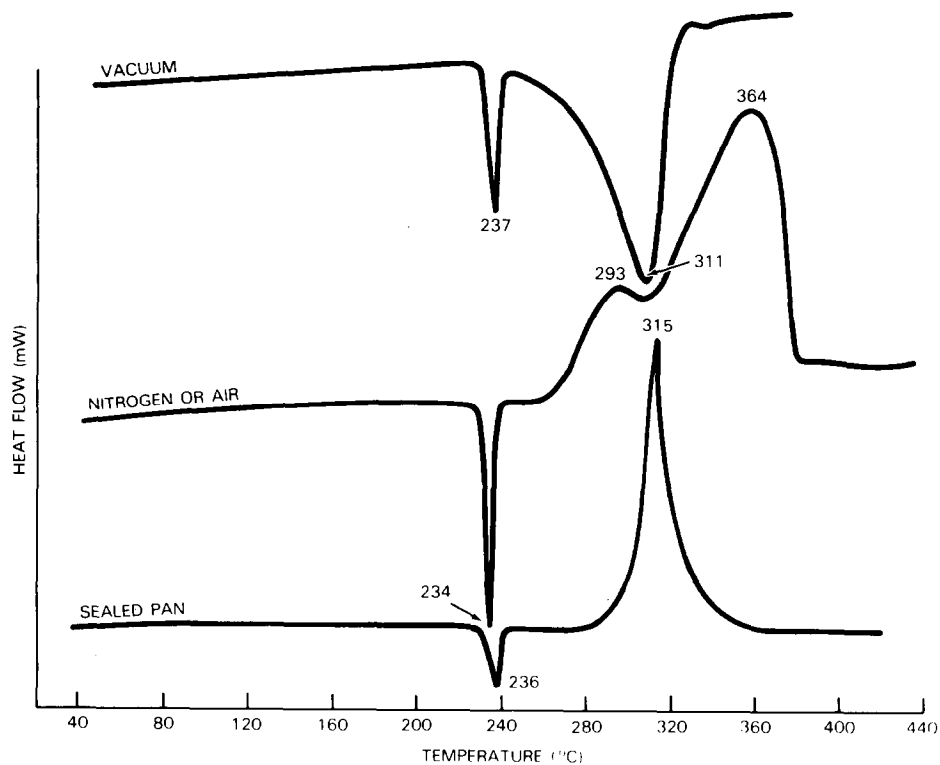


Fig. 18. DSC curves for AP at $5^{\circ}\text{C min}^{-1}$.

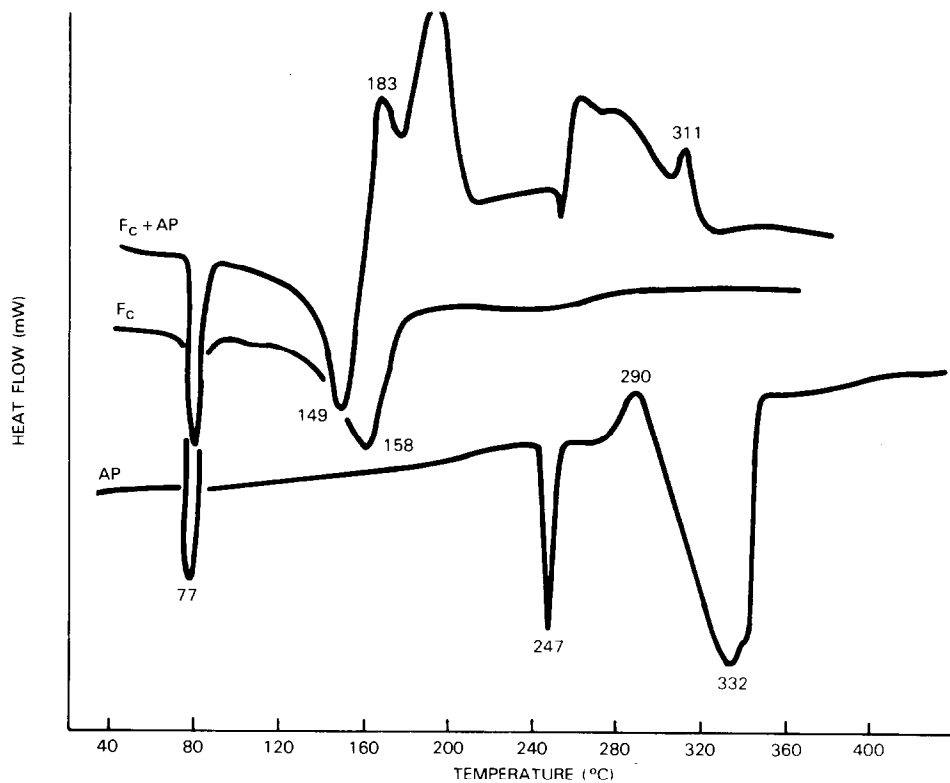


Fig. 19. DSC curves of ferrocenyl(dimethylaminoethyl)ketone/AP (w/w) at $10^{\circ}\text{C min}^{-1}$ in vacuum.

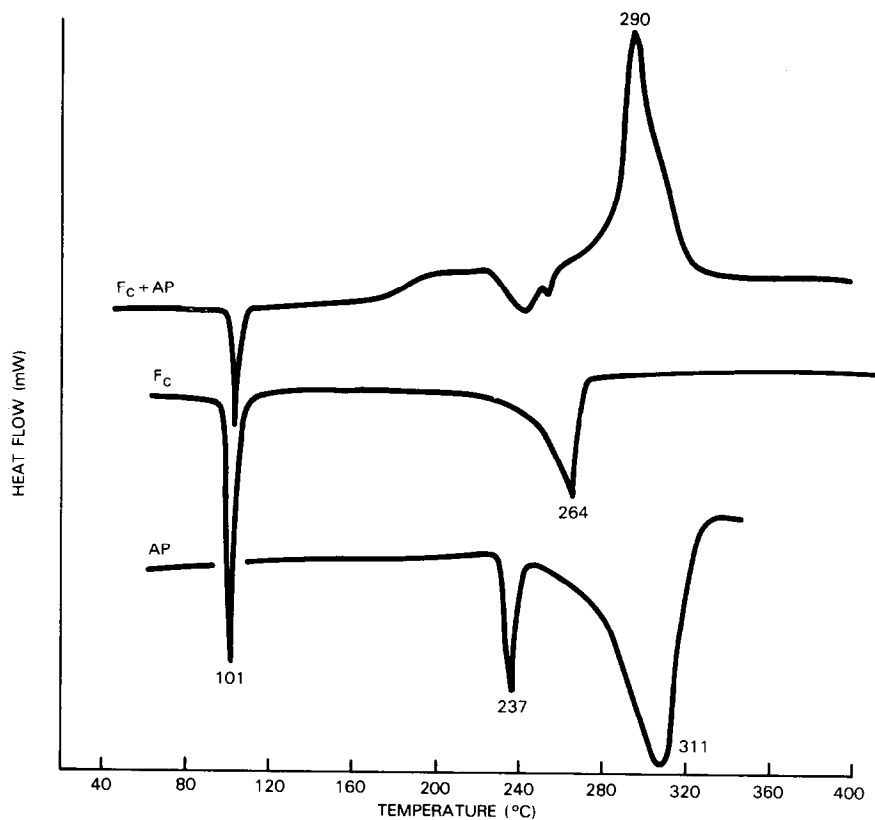


Fig. 20. DSC curves of bis(2-ferrocenylethyl)disulfide/AP (w/w) at $5^{\circ}\text{C min}^{-1}$ in vacuum.

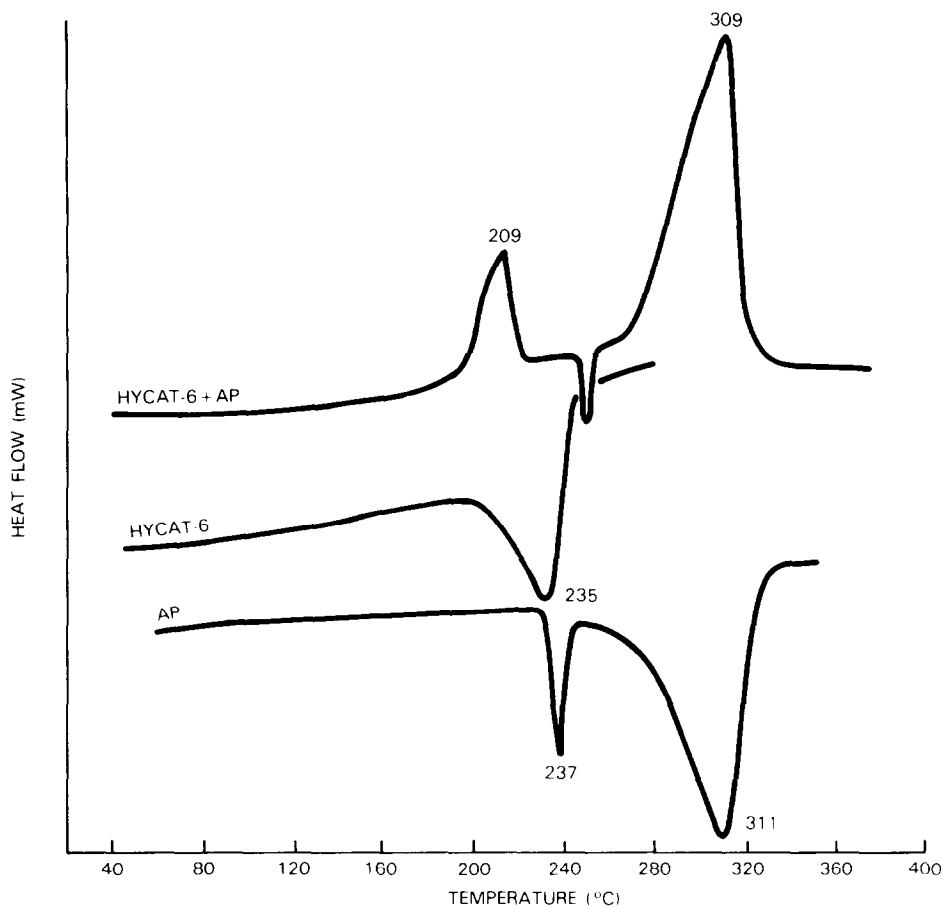


Fig. 21. DSC curves of Hycat-6/AP (w/w) at $5^{\circ}\text{C min}^{-1}$ in vacuum.

TABLE 2

Dynamic DSC kinetic data in vacuum for thermal decomposition of ferrocenyl compounds with/without AP

Compound	E^a	$\log A^b$	$\tau_{0.5}^c$
bis(2-Ferrocenylethyl)disulfide	29.4	11.80	20 y
bis(2-Ferrocenylethyl)disulfide + AP	23.7	9.05	2.5 y
Hycat-6	22.9	9.71	60 d
Hycat-6 + AP	15.8	7.16	14 h
Catocene	23.0	9.84	49 d
Catocene + AP	18.1	8.25	33 h
AP	21.2	7.57	2 y

^a E is the activation energy (kcal/mol^{-1}).

^b $\log A$ is the Arrhenius frequency factor (min^{-1}).

^c $\tau_{0.5}$ is the half-life for a first order reaction at 150°F and a vacuum of 5 mm. h, hour; d, day; y, year.

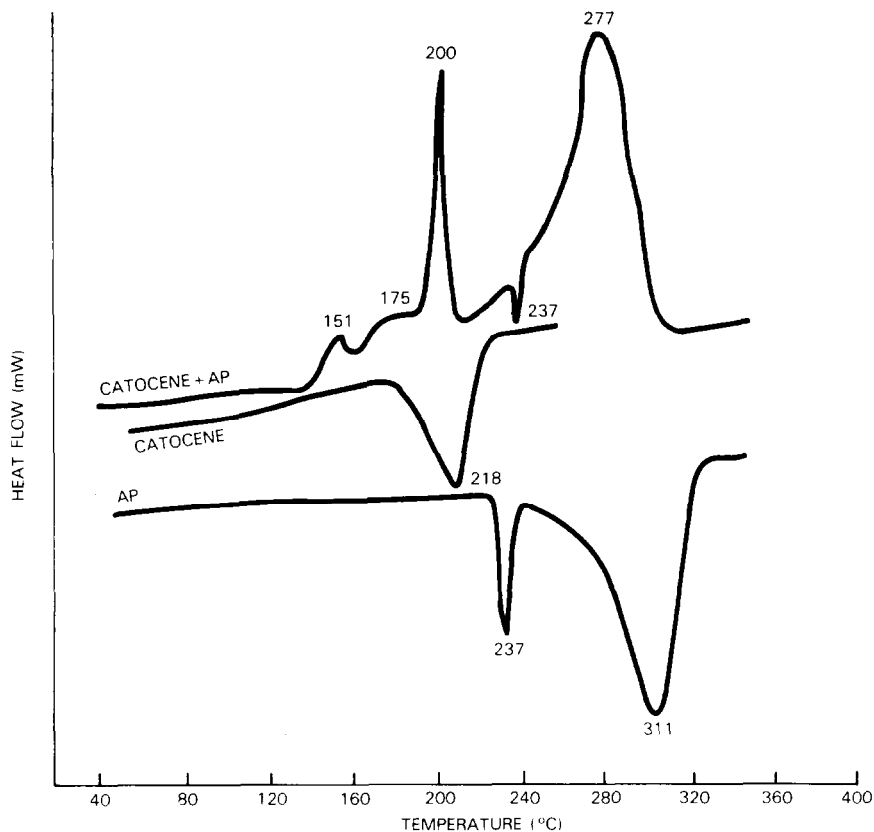


Fig. 22. DSC curves of Catocene/AP (w/w) at $5^{\circ}\text{C min}^{-1}$ in vacuum.

pellets in vacuum [13,14] an activation energy of $21.5 \text{ kcal mol}^{-1}$ was calculated for the sublimation of AP under low pressure [15] and that sublimation and decomposition processes occurred simultaneously at ambient pressure, however, if the pressure is decreased then the sublimation process [16,17] is favored. The present values for the activation energy for the sublimation process are in very good agreement with those reported using other techniques.

Figures 19 to 22 show DSC curves in vacuum for four ferrocenyl compounds and their admixtures with AP. The solid ferrocenyl compounds in Figs. 19 and 20 show melting peaks followed by endothermic decomposition peaks and the liquid ferrocenyl compounds in Figs. 21 and 22 show endothermic volatilization/decomposition peaks. The admixtures indicate that an interaction is occurring between the two ingredients. The ferrocenyl compound in the mixture does not have an endothermic decomposition peak but an exothermic peak which comes at a lower temperature than the endothermic decomposition peak of the neat ferrocenyl compound. Ammonium perchlorate in the mixture does not show an endothermic sublima-

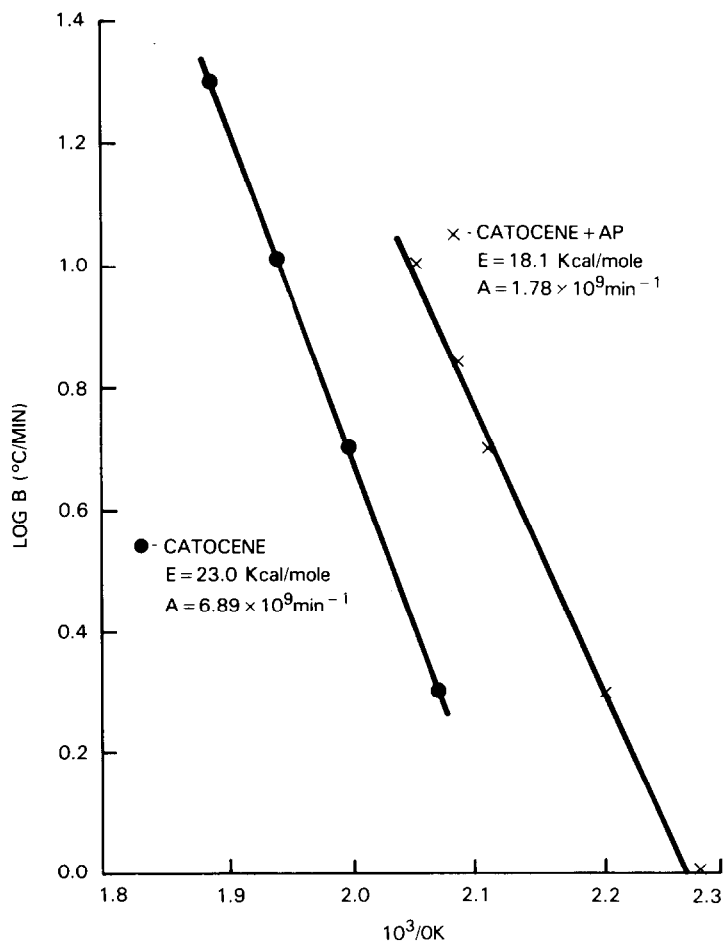


Fig. 23. DSC variable heating rate plot for the thermal decomposition of Catocene/AP (w/w).

tion peak but an exothermic decomposition peak which comes at a lower temperature than that observed for neat AP.

Kinetic data for the thermal decomposition of the neat ferrocenyl compound and for the ferrocenyl component in the admixtures were determined by a DSC variable heating rate method. A typical plot of log heating rate vs. reciprocal of the absolute peak temperature is given in Fig. 23 for Catocene/AP (w/w). Activation energy data are given in Table 2. In the admixture the activation energy for the thermal decomposition of the ferrocenyl component was lowered by 20% which caused a dramatic decrease in the calculated half-life of the material in a vacuum at 150°F. Good agreement was found for the activation energy for the thermal decomposition in vacuum of the neat ferrocenyl compounds by isothermal TG and dynamic DSC methods.

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