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AFRPL-TR-67-165

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COMBUSTION MECHANISM
OF
HIGH BURNING RATE SOLID PROPELLANTS

Contract F04611-67-C-0034

QUARTERLY TECHNICAL REPORT AFRPL-TR-67-165
June 1967

David A. Flanigan
Huntsville Division
Thiokol Chemical Corporation

Air Force Rocket Propulsion Laboratory
Research and Technical Division
Air Force Systems Command
United States Air Force
Edwards Air Force Base, California 93523

NOTICES

(UNCLASSIFIED)

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FOREWORD

(U) This, the second Quarterly Technical Report under Contract No. F04611-67-C-0034, covers the work performed from 1 March through 31 May 1967. This contract with the Huntsville Division of Thiokol Chemical Corporation was initiated under Air Force Rocket Propulsion Laboratory, Research and Technology Division Project Number 3148. It is being accomplished under the technical direction of R. W. Bargmeyer, 1/Lt., USAF of the Research and Technology Division, Air Force Systems Command, United States Air Force, Edwards Air Force Base, California 93523.

(U) Dr. David A. Flanigan of Thiokol's Research and Development Department is the Principal Investigator and Mr. Carl J. Whelchel of the Project Management Directorate is Assistant Project Manager for this program. Full authority for the management control of this program is the responsibility of Mr. G. F. Mangum of the Project Management Directorate. Others who cooperated in the work and in the preparation of this report are Messrs. B. A. Allen, C. S. Combs, C. I. Ashmore and Mrs. E. J. Grice.

(U) This report has been assigned the Thiokol internal number 39-67 (Control No. C-67-39A).

(U) This project is being accomplished as a part of the Air Force program, the overall objective of which is to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from 1 to 10 inches per second. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing guideline properties determined under Contract AF04(611)-11212 toward development of an ideal catalyst. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients.

(U) This report contains no classified information extracted from other classified documents.

STATEMENT OF APPROVAL

(U) Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. EBELKE, Col., USAF
Chief, Propellants Division
Air Force Rocket Propulsion Laboratory

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CONFIDENTIAL ABSTRACT

(C) Thiokol's program to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from 1 to 10 inches per second is divided into three phases: Phase I - Synthesis of Burning Rate Catalysts, Phase II Decomposition Studies and Evaluation of Catalysts and Phase III - Decomposition of Advanced Oxidizers, Fuels, and Binders. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing already determined guideline properties toward development of an ideal catalyst under Phases I and II. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients. To date, 30 candidate catalyst materials have been synthesized and the physical properties ascertained. Compatibility testing of these materials is essentially complete and no serious problems are expected in the formulation and scale-up of propellants containing the candidate catalysts. Burn rate studies thus far indicate that several prospective liquid ferrocene derivatives offer considerable potential in increasing burn rates over that presently available with n-butyl ferrocene [PLASTISCAT -IV$^{(R)}$].

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SECTION I

INTRODUCTION

(U) The objective of this program is to tailor the burning rate of a propellant predictably and controllably, to any desired level in the range from 1 to 10 inches per second. Ballistic and mechanical properties of propellants studied will be maintained at the state-of-the-art standards of current Minuteman propellant.

(C) Thiokol's approach to obtain the program objective will be through the continued investigation of iron compound effects on the aluminum-ammonium perchlorate-polybutadiene binder system. It is also designed to systematically evaluate new propellant ingredients as to their effect on burning rate and the related effect on combustion mechanism. New materials which will be evaluated are hydroxyl-ammonium perchlorate, hydrazine diperchlorate and nitronium perchlorate oxidizers; aluminum hydride, beryllium, beryllium hydride fuels; P-BEP, NFPA polymers, and TVOPA plasticizer. The data and conclusions reached under Contract AF04(611)-11212 will be used as a base line guide for the work to be accomplished under this program.

(U) The planned program consists of three major areas: synthesis, evaluation, and advanced ingredient studies. It is designed to progress in a logical manner so that the most promising materials receive the more extensive evaluation and the less desirable materials are discarded at an early date. The three phases of the program are:

(U) Phase 1 - Synthesis of Burning Rate Catalysts

(U) Burning rate catalysts will be synthesized for use in the AP/Al/PB propellant system. Prior knowledge as a propulsion contractor and the data obtained from Contract AF04(611)-11212 will serve as base line guides. As a new material is synthesized, it will be evaluated in Phase II.

(U) Phase II - Decomposition Studies and Evaluation of Catalysts

(U) An evaluation of the compatibility of the candidate catalysts with other propellant ingredients will be accomplished upon completion of synthesis, elemental characterization, and physical property determination of each candidate material. Data obtained in this phase will allow recommendations to be made relative to the development of new burning rate catalysts and the development of high burning rate propellants utilizing the improved catalyst.

(U) Phase III - Decomposition of Advanced Oxidizers, Fuels, and Binders

(U) Phase III effort will be directed toward obtaining a basic fundamental knowledge of the decomposition of advanced fuels, oxidizers, and binders. Laboratory test data will be utilized to postulate a burning mechanism of the advanced ingredient and a comparison made with that of conventional propellant ingredients.

(U) This report covers work performed for the period 1 March through 31 May 1967 under Contract F04611-67-C-0034. Effort to date has been concerned solely with Phases 1 and II, which are being conducted concurrently. Phase III will be initiated after the completion of Phases I and II.

SECTION II

EXPERIMENTAL ACCOMPLISHMENTS

(U) Based on the results of effort expended under Contract AF04(611)-11212, the experiments under this program will be directed toward the synthesis and characterization of more efficient burn rate catalysts.

(U) 1. Phase I - Synthesis of Burning Rate Catalysts

(U) The guidelines for synthesis of more efficient burn rate catalysts have been derived from effort conducted under the above contract and are listed below:

> High iron content
> Wide liquid range
> Readily oxidizable
> Compatible with other propellant ingredients
> Maximum fuel content (heat release on oxidation)

(U) The synthesis of newer burn rate catalyst will be directed toward maximizing the aforementioned properties into the ideal catalyst. Effort performed in this area of research during this reporting period is presented in subsequent paragraphs.

(U) Preliminary synthesis effort has afforded a series of both liquid and solid ferrocene containing compounds which have been evaluated as candidate burn rate catalysts. A list of the compounds as well as their physical constants is shown in Table I.

(U) During this report period, further synthesis effort has been accomplished with the following results:

(C) The reaction of hydroxymethyl ferrocene with ethanol in the presence of an acid catalyst gave ethoxymethyl ferrocene (b. p. 88° C/0.15 mm).

Reaction:

(C) $Fc\,CH_2\,OH + CH_3\,CH_2\,OH \longrightarrow Fc\,CH_2\,OCH_2\,CH_3$
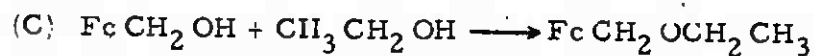
TABLE I

PHYSICAL CONSTANTS OF CATALYSTS EVALUATED

Compound	M.p., °C	B.p., °C	Theo. %Fe	Theo. %Cu
Dimethylaminomethyl ferrocene	---	78/0.02 mm	23	---
Propargyl ferrocenoate	81-84 (dec.)	---	21	---
Allyl ferrocenoate	36-36.5	122/0.15 mm	21	---
n-Propyl ferrocenoate	---	96/0.10 mm	21	---
1,3-Diferrocenyl-1-oxo-2-propene	198-199	---	26	---
Sodium salt of β-ferrocenyl-β-oxo propionaldehyde	240-242 (dec.)	---	20	---
1,3-Diferrocenyl-1,3-propanedione	215 (dec.)	---	25	---
Copper complex of 1,3-diferrocenyl-1,3-propanedione	280 (dec.)	---	24	7
2-methoxyethyl ferrocenoate	34-35	---	19	---
Copper (I) complex of β-ferrocenyl-β-oxopropion-aldehyde	224-225 (dec.)	---	18	20
Copper (II) complex of β-ferrocenyl-β-oxopropion-aldehyde	200 (dec.)	---	20	11
Methoxy methyl ferrocene	---	66/0.025	24	---
1,1'-Di(methoxy methyl) ferrocene	---	310	20	---
1-Hydroxy methyl-1'-methoxy methyl ferrocene	---	280	22	---
Trimethoxy iron	>300	---	38	---

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(U) Bisferrocenylmethyl ether (m. p. 126 - 129° C; Lit[1] 130 - 131° C) was prepared by the addition of acid catalyst to an ethereal solution of hydroxymethyl ferrocene.

Reaction:

(C) $2 \, Fc \, CH_2 \, OH \longrightarrow Fc \, CH_2 \, OCH_2 \, Fc$

(U) Allyloxymethyl ferrocene [b. p., 260° C (DTA)] was prepared by the reaction of hydroxymethyl ferrocene with allyl alcohol in the presence of acid.

Reaction:

(C) $Fc \, CH_2 \, OH + CH_2 = CH \, CH_2 \, OH \longrightarrow Fc \, CH_2 \, OCH_2 \, CH = CH_2$
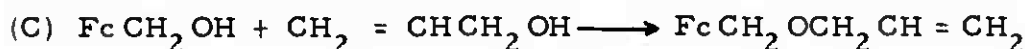
(U) Bis (α - ferrocenylethyl) ether [b. p. 197° C, 232° C (dec.) (DTA)] was prepared by the reaction of α - hydroxyethyl ferrocene with an acid catalyst.

Reaction:

(C) $2 \, Fc \, CH(CH_3) \, OH \longrightarrow Fc \, CH(CH_3) \, OCH(CH_3) \, Fc$
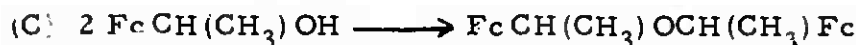
(C) Attempts to prepare triferrocenylmethoxy iron by the reaction of hydroxymethyl ferrocene with ferric chloride gave bisferrocenylmethyl ether (ca. 3 percent yield) and an equal amount of a brown solid, which melted at 99 - 101° C. The infrared spectrum did not rule out triferrocenylmethoxy iron, but the difficulty involved in isolation of this compound and the low yield obtained discourage further investigation of this compound as a serious candidate.

(C) Esterification of ferrocenylacetic acid with methanol gave methyl ferrocenylacetate [b. p. 282° C (DTA)].

Reaction:

(C) $Fc \, CH_2 \, CO_2 \, H + CH_3 \, OH_2 \, OH \longrightarrow Fc \, CH_2 \, CO_2 \, CH_2 \, CH_3$

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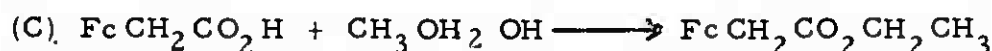
1. E. G. P. evalova, Yu. A. Ustynyuk, and A. N. Nesmeyanov, Izv. Akad. Nauk SSS.. Ser. Khim., No. 11, 1972 (1963), (English Translation). Also see C. R. Hauser and C. E. Cain, J. Org. Chem., 23, 2007 (1958).

Substitution of ethanol in this preparation afforded ethyl ferrocenylacetate [b.p. 286° C (DTA)].

Reaction:

(C) $Fc\,CH_2\,CO_2\,H + CH_3\,OH_2\,OH \longrightarrow Fc\,CH_2\,CO_2\,CH_2\,CH_3$
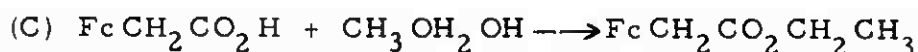
(C) Attempted purification of the products using base-washed alumina was not successful as they turned dark brown on the column. Acid-washed alumina, however, has been successfully employed with no apparent ill effects.

(C) The reaction of hydroxymethyl ferrocene with butyl mercaptan in the presence of an acid catalyst gave n-butylthiomethyl ferrocene [b.p. 274° C, 300° C (dec.) (DTA)].

Reaction:

(C) $Fc\,CH_2\,OH + CH_3\,(CH_2)_3\,SH \longrightarrow Fc\,CH_2\,S\,(CH_2)_3\,CH_3$
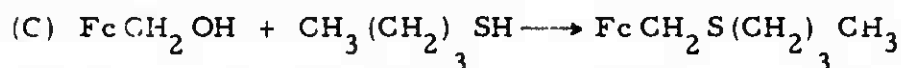
(C) The reaction of 1,1'-dihydroxymethyl ferrocene with methanol and water (acetic acid catalyst) gives a mixture of 1,1'-dimethoxymethyl ferrocene and 1-hydroxymethyl-1'-methoxymethyl ferrocene (previously reported). This material has been subjected to low temperatures for extended periods ($+10^{\circ}$ C for 24 hours; -10° C for 72 hours; -40° C for 48 hours) and has, thus far, failed to freeze. It should be noted that the material was exposed to the above temperatures in the order given and the cooling was, therefore, fairly gradual.

(C) Reaction of hydroxymethyl ferrocene with acetic acid gave ferrocenyl-methyl acetate (m.p., 75 to 77° C) in good yield.

(C) $Fc\,CH_2\,OH + CH_3\,CO_2\,H \longrightarrow CH_3\,CO_2\,CH_2\,Fc$
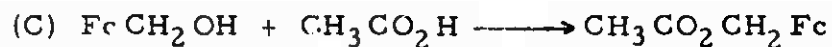
(C) The reaction of hydroxymethyl ferrocene with ferrocenoic acid in acetone afforded ferrocenylmethyl ferrocenoate (m.p. 131 to 135° C).

(C) $Fc\,CH_2\,OH + Fc\,CO_2\,H \longrightarrow Fc\,CO_2\,CH_2\,Fc$
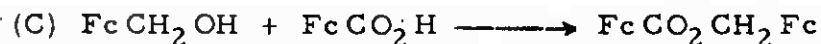
(C) An attempt was made to prepare ferrocenoylacetic acid by reaction of acetylferrocene with sodamide and subsequent carboxylation of the resulting carbon ion.

(C) $Fc\,COCH_3 \xrightarrow{Na\,NH_2} Fc\,COCH_2^- \xrightarrow[2.\,H^+]{-1.\,CO_2} Fc\,COCH_2\,CO_2\,H$

Starting material was recovered.

(C) β -(Ferrocenylmethylthio) propionic acid (m. p., 80 to 81°) was prepared by reaction of hydroxymethyl ferrocene with β -mercaptopropionic acid in water.

(C) $Fc\,CH_2\,OH + HS\,CH_2\,CH_2\,CO_2\,H \longrightarrow Fc\,CH_2\,S\,CH_2\,CH_2\,CO_2\,H$
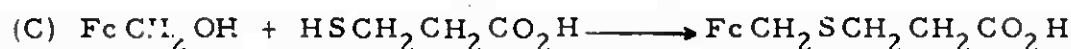
(C) Esterification with methanol afforded methyl β -(ferrocenylmethylthio) propionate [b. p., 260° C (DTA)] in good yield.

(C) $Fc\,CH_2\,SCH_2\,CH_2\,CO_2\,H + CH_3 + CH_3\,OH \xrightarrow{H+} Fc\,CH_2\,SCH_2\,CH_2\,CO_2\,CH_3$
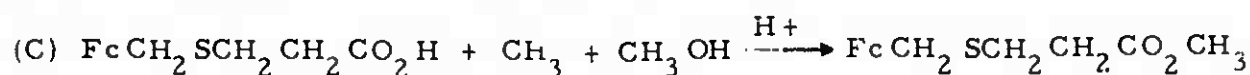
(C) Reaction of hydroxymethyl ferrocene with mercaptoethanol in water gave β -(ferrocenylmethylthio) ethanol (b. p., 290° C) in high yield.

(C) $Fc\,CH_2\,OH + HO\,CH_2\,CH_2\,SH \longrightarrow Fc\,CH_2\,S\,CH_2\,CH_2\,OH$
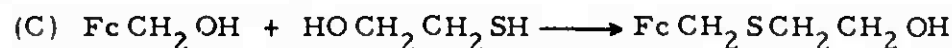
(C) The condensation polymerization of 1, 1'-dihydroxymethyl ferrocene with a slight excess of 1, 2-dimercaptoethane in water yielded mercaptomethyl terminated poly- [bis (methylthiomethyl) ferrocene] (denoted poly F S -1) (m. p., 119 to 122° C).

(C) $Fc\,(CH_2\,OH)_2 + HS\,CH_2\,CH_2\,SH \longrightarrow [Fc\,(CH_2\,S\,CH_2\text{-})_2]_x\,(\text{-}CH_2\,SH)_2$
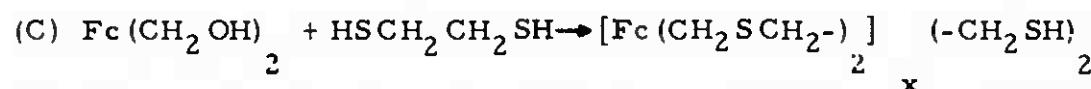
(U) The structural assignments of the above catalysts were confirmed by infrared analysis. The physical constants are as follows:

Compound	M.p., $^{\circ}$C	B.p., $^{\circ}$C	Theor. % Fe
Ethoxymethyl Ferrocene	---	88/0.15	23
Bisferrocenylmethyl Ether	126-129	---	27
Allyloxymethyl Ferrocene	---	260	22
Bis (α ferrocenylethyl) Ether	---	197, 232 (dec)	25
Ferrocenylmethyl acetate	75-77	---	22
Ferrocenylmethyl ferrocenoate	131-135	---	26
β - (Ferrocenylmethylthio) propionic acid	80-81	---	18
Methyl β - (ferrocenylmethylthio) propionate	260 (DTA)	---	18
β - (Ferrocenylmethylthio) ethanol	290 (DTA)	---	20
poly F S -1	119-122	---	16
Methyl ferrocenylacetate	---	282	22
Ethyl ferrocenylacetate	---	286	21
n-Butylthiomethyl ferrocene	---	274, 300 (dec)	19

(U) It has been determined that the freezing points of compounds recorded in the first quarterly technical report (AFRPL-TR-67-99, March 1967) are in error. Many of the compounds froze when held for a number of hours at temperatures substantially higher than their reported freezing points. The freezing points were obtained by conventional methods. Failure to reach equilibrium at moderate rates of cooling (ca. 2°/min.) can possibly be attributed to the high viscosity of these compounds at low temperatures and substantial super cooling. Only melting points will be reported in the future, since the melting point of a compound is less time-dependent than the freezing point.

(C) The time dependence of freezing in this type of compound is substantial. For example, PLASTISCAT-IV[R] has a melting point of 8 to 11° C, but the freezing point was determined to be -25 to -34° C. PLASTISCAT-IV[R] froze when held at 10° C for a number of hours.

(U) An accurate determination of the melting point of each compound synthesized is now in progress.

(U) Compounds prepared during this program for which analyses have been obtained are as follows:

(U) $FcCO_2CH_2C = CH$ (propargyl ferrocenate)

(C) Analysis calculated for $C_{14}H_{12}FeO_2$:   C, 62.72; H, 4.51; Fe, 20.83.

Found: C, 62.96; H, 4.64; Fe, 21.07.

(U) $FcCO_2CH_2CH_2CH_3$ (n-propyl ferrocenate)

(C) Analysis calculated for $C_{14}H_{16}FeO_2$:   C, 61.79; H, 5.93; Fe, 20.52.

Found: C, 62.04; H, 6.16; Fe, 19.8.

(U) $FcCH_2OCH_3$ (methoxymethyl ferrocene)

(C) Analysis calculated for $C_{12}H_{14}FeO$: C, 62.64; H, 6.13; Fe, 24.27.

Found: C, 62.94; H, 6.30; Fe, 24.55.

(U) $CH_3OCH_2FcCH_2OH$ (1-hydroxymethyl-1^1-methoxymethyl ferrocene)

(C) Analysis calculated for $C_{13}H_{17}FeO_2$: C, 60.05; H, 6.20; Fe, 21.48.

Found: C, 59.72, H, 6.46; Fe, 21.10.

(U) $Fc(CH_2OCH_3)_2$ [1,1^1-di(methoxymethyl) ferrocene]

(C) Analysis calculated for $C_{14}H_{19}FeO_2$: C, 61.36; H, 6.62; Fe, 20.38.

Found: C, 61.31; H, 6.81; Fe, 20.21.

(U) $CH_3CO_2CH_2Fc$ (ferrocenyl methyl acetate)

(C) Analysis calculated for $C_{13}H_{14}FeO_2$:   C, 60.49; H, 5.47; Fe, 21.64.

Found: C, 60.75; H, 5.56; Fe, 21.95.

(U) $FcCH_2CO_2CH_2CH_3$ (ethyl ferrocenylacetate)

(C) Calculation for $C_{14}H_{16}FeO_2$:   C, 62.25; H, 5.22; Fe, 20.68.

Found: C, 62.59; H. 5.58; Fe, 20.94.

(U) $FcCH_2S(CH_2)_3CH_3$ (a-butylthiomethyl ferrocene)

(C) Analysis calculated for $C_{15}H_{20}FcS$: C, 62.50; H, 6.99; Fe, 19.38.

Found: C, 62.18; H, 6.86; Fe, 19.50.

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(U) $C_{14}H_{16}FeO$ (allyloxy methyl ferrocene)

(C) Calculated for $C_{14}H_{16}FeO$: C, 65.65; H, 6.30.

Found: C, 65.80; H, 6.58.

(U) $FcCH_2OCH_2CH_3$ (exthoxymethyl ferrocene)

(C) Analysis calculated for $C_{13}H_{16}FeO$:

C, 63.96; H, 6.67; Fe, 22.88; Mol. Wt., 244.

Found: C, 64.06; H, 6.72; Fe, 22.84; Mol. Wt., 240.

(U) $FcCH(CH_3)OCH(CH_3)Fc$ [Bis (ᴣ-ferrocenylethyl) ether]

(C) Analysis calculated for $C_{24}H_{26}Fe_2O$: C, 65.19; H, 5.93; Fe, 25.26.

Found: C, 65.47; H, 6.09; Fe, 25.23.

(U) During this reporting period effort was expended to prepare substantial amounts of hydroxymethyl ferrocene. This compound is a necessary precursor to many of the more promising candidates, and at present the pure compound cannot be purchased at a reasonable price. To date 0.5-pound of this compound has been prepared.

(U) 2. Phase II - Decomposition Studies and Catalyst Evaluation

(U) Upon completion of synthesis, elemental characterization and physical property determination of each candidate catalyst, an evaluation of the compatibility of the candidate catalysts with other propellant ingredients will be accomplished. Following the compatibility, the actual effectiveness of the candidate catalysts will be measured by determining the propellant processing characteristics as well as the burning rate.

(U) a. Catalyst Compatibility Studies

(C) Compatibility testing at ambient temperatures and at 160° F between catalyst candidates and ammonium perchlorate, CTPB binder, curing agents and aluminum were reported in Quarterly Technical Report AFRPL-TR-67-99 (March 1967). In summary, no serious incompatibility problems were noted with the exception of dimethylaminomethyl ferrocene, which at mix temperature ($120 - 160^\circ$ F), reacted with the oxidizer to liberate ammonia and served as a base catalyst for the exothermic polymerization of MAPO.

(U) The major effort during this report period was to test the compatibility of ammonium perchlorate and candidate catalysts at elevated temperatures (mixing and cure temperatures) for periods up to ten days. The differences noted in the differential thermal analyses (DTA) of oxidizer-catalyst mixtures after 10 days gave a strong indication as to whether catalyst oxidation could possibly occur during a cure cycle. It should be pointed out that the test is considerably more severe than that which would be encountered in an actual propellant. In essence, it was believed that if ignition or at least exothermic decomposition did not occur in these tests, no problem should be expected in the propellant.

(C) Ammonium perchlorate containing 5 percent catalyst (by weight) was subjected to a temperature of 160° F for ten days. The catalysts evaluated are those listed in Table I. Visual observations show no apparent change in color of any catalyst/ammonium perchlorate mixture, except for methoxymethyl ferrocene, which apparently oxidized extensively, and 2 - methoxyethyl ferrocenate, which changed color from orange to lemon. Microscopic examinations showed particles of red iron oxide (Fe_2O_3) in the methoxymethyl ferrocene/ammonium perchlorate mixture and the color change of 2 - methoxyethyl ferrocenate may simply be attributed to dilution by ammonium perchlorate.

(U) Ammonium perchlorate standard grind (50-55μ weight mean diameter) was selected to provide more intimate surface contact, especially with the solid catalysts, and thus provide a more severe test of compatibility.

(C) After ten days at a temperature of 160° F, a differential thermal analysis of these oxidizer catalyst mixtures was obtained. A control sample of standard grind ammonium perchlorate was subjected to the same conditions as the catalyst/oxidizer mixtures (Figure 1). The DTA plot of trimethoxy iron exhibited no change from original unaged values. The remainder of the catalysts examined seemingly showed some signs of interaction. Probably the most significant change was noted with methoxymethyl ferrocene (Figure 2). The reduction in intensity of the peak at 182° C supports the previously mentioned postulation that oxidation has occurred. In essence, the peak at 182° C can be attributed to oxidation of the methoxymethyl ferrocene by the small amount of oxidizer decomposition gases present at 160° F. Figures 3 through 13 show the differential thermal analyses of the rest of the oxidizer/catalyst mixtures. At this point, it is believed that many of the variations observed following aging can be attributed mainly to slight oxidation and improved dispersion of the catalyst in the oxidizer during the aging process. No chemical explanation is available at this time for some of the new peaks and disappearance of others.

(C) In order to determine how serious these interactions might be and to ascertain the degree of the interaction, the catalyst, after being in contact with the oxidizer for 10 days at 160° F, was subjected to thin layer chroma-

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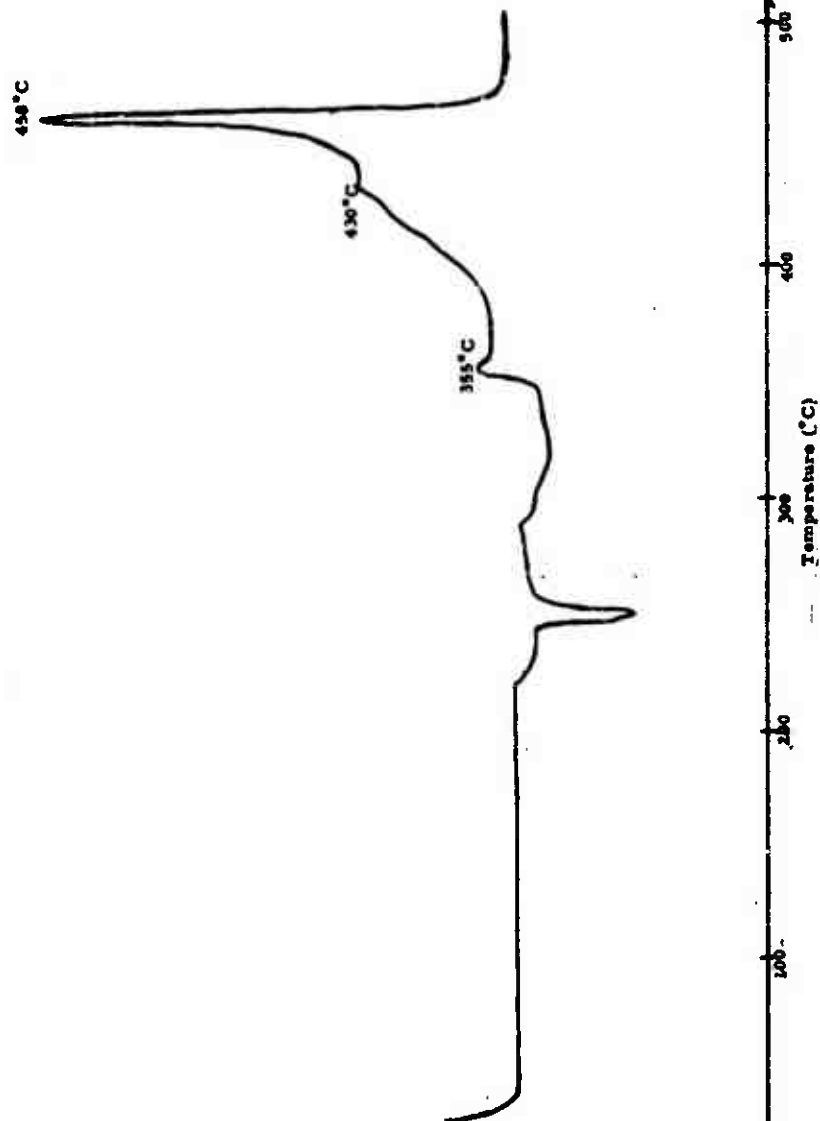
Figure 1. DTA of Standard Grind AP (50-55 Micron WMD) Control After 10 Days at 160°F.
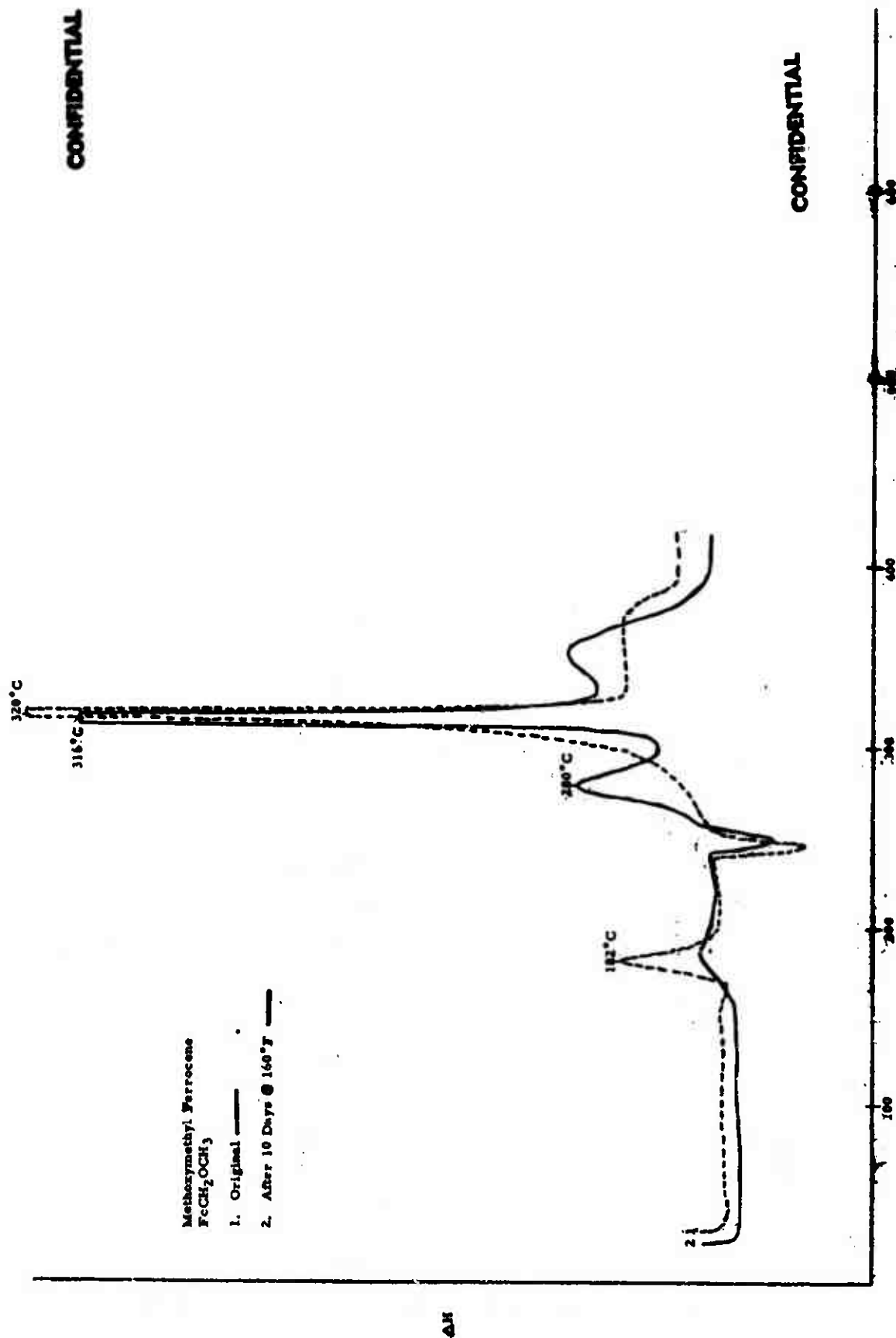
Figure 2. DTA of AP (Standard Grind)+ 5 Percent Catalyst (Methoxymethyl Ferrocene).

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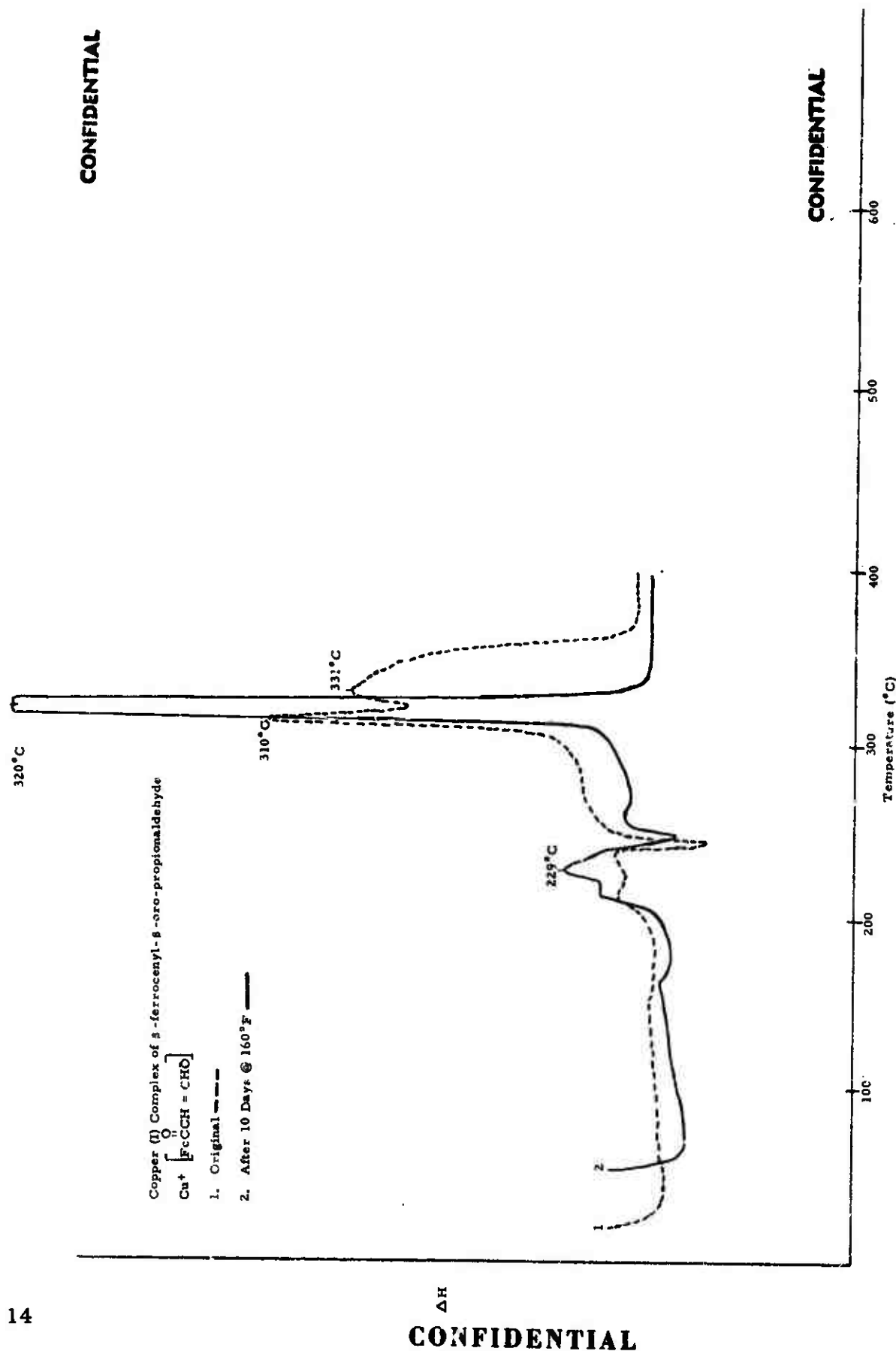
Figure 3. DTA of AP (Standard Grind) + 5 Percent Catalyst - Copper (II) Complex of β-Ferrocenyl-β-oxo-propionaldehyde.

Copper (I) Complex of s-ferrocenyl-β-oxo-propionaldehyde

Cu⁺ [FcCCH = CHO]

1. Original
2. After 10 Days @ 160°F

320°C
310°C
331°C
229°C

Temperature (°C)

ΔH

14

Copper (II) Complex of β -ferrocenyl- β -oxo-propionaldehyde

Cu⁺⁺ FcCOCH=CHO⁻ 2

1. Original ————
2. After 10 Days @ 160°F ————

321°C

318.5°C

329°C

ΔH

Temperature (°C)

100   200   300   400   500   600
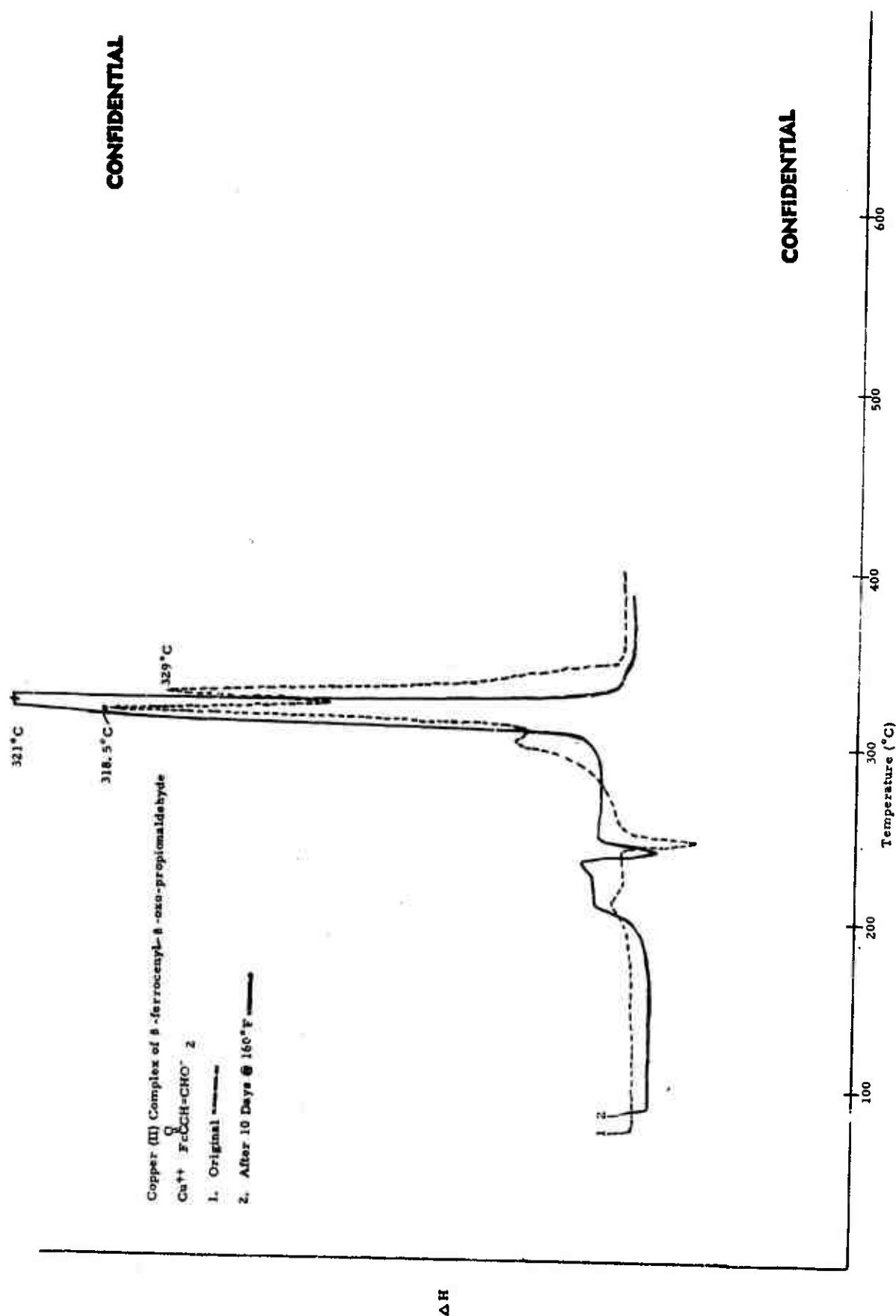
Figure 4. DTA of Copper (II) Complex of β-Ferrocenyl-β-oxo-propionaldehyde.
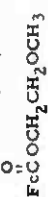
Figure 5. DTA of 2-Methoxyethyl Ferrocenoate.

2 - Methoxyethyl Ferrocenoate

$FcCOCH_2CH_2OCH_3$

1. Original ━━━

2. After 10 Days @ 160°C ━━━
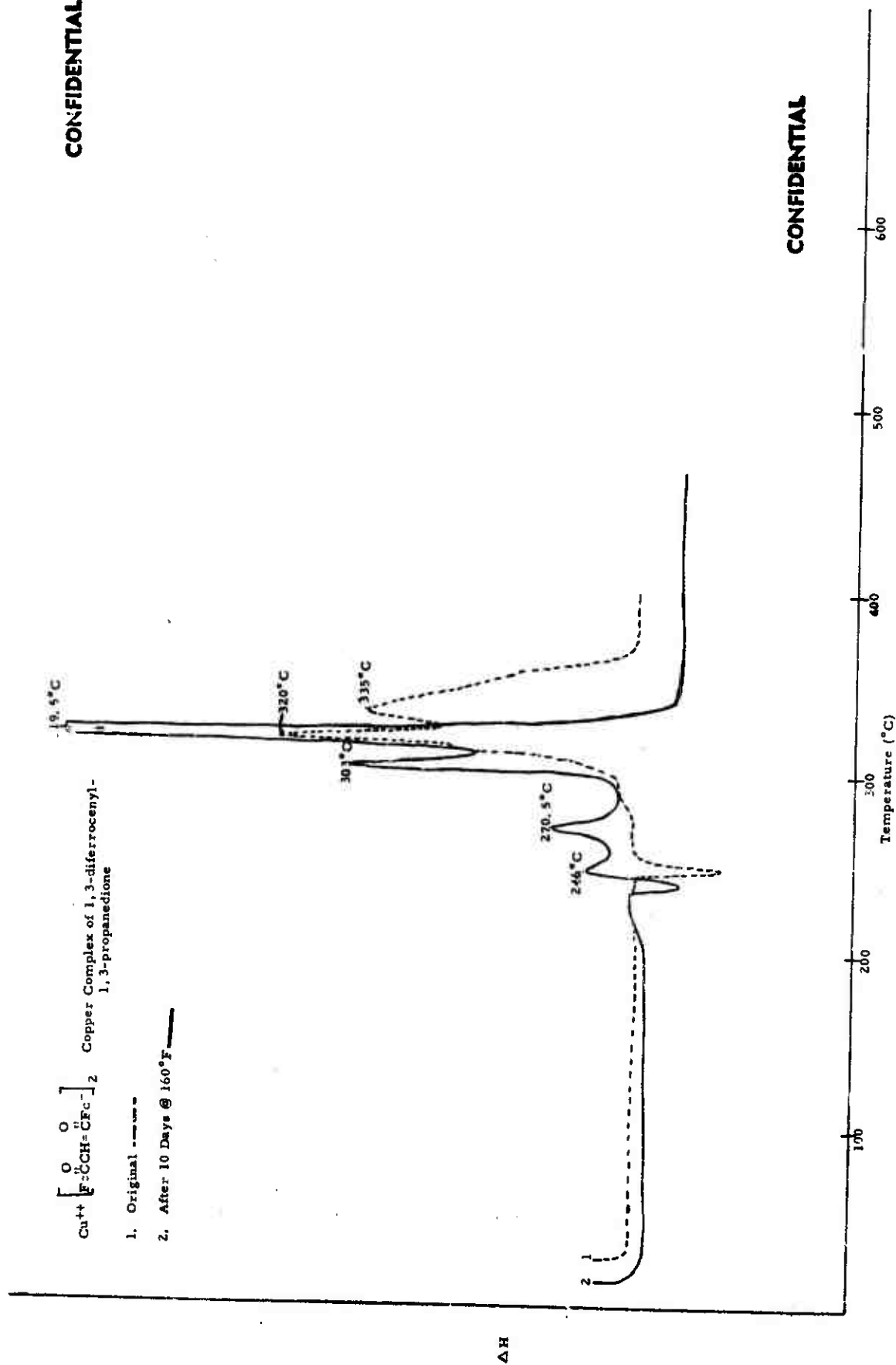
Figure 6. DTA of Copper Complex of 1,3-diferrocenyl-1,3-propanedione.
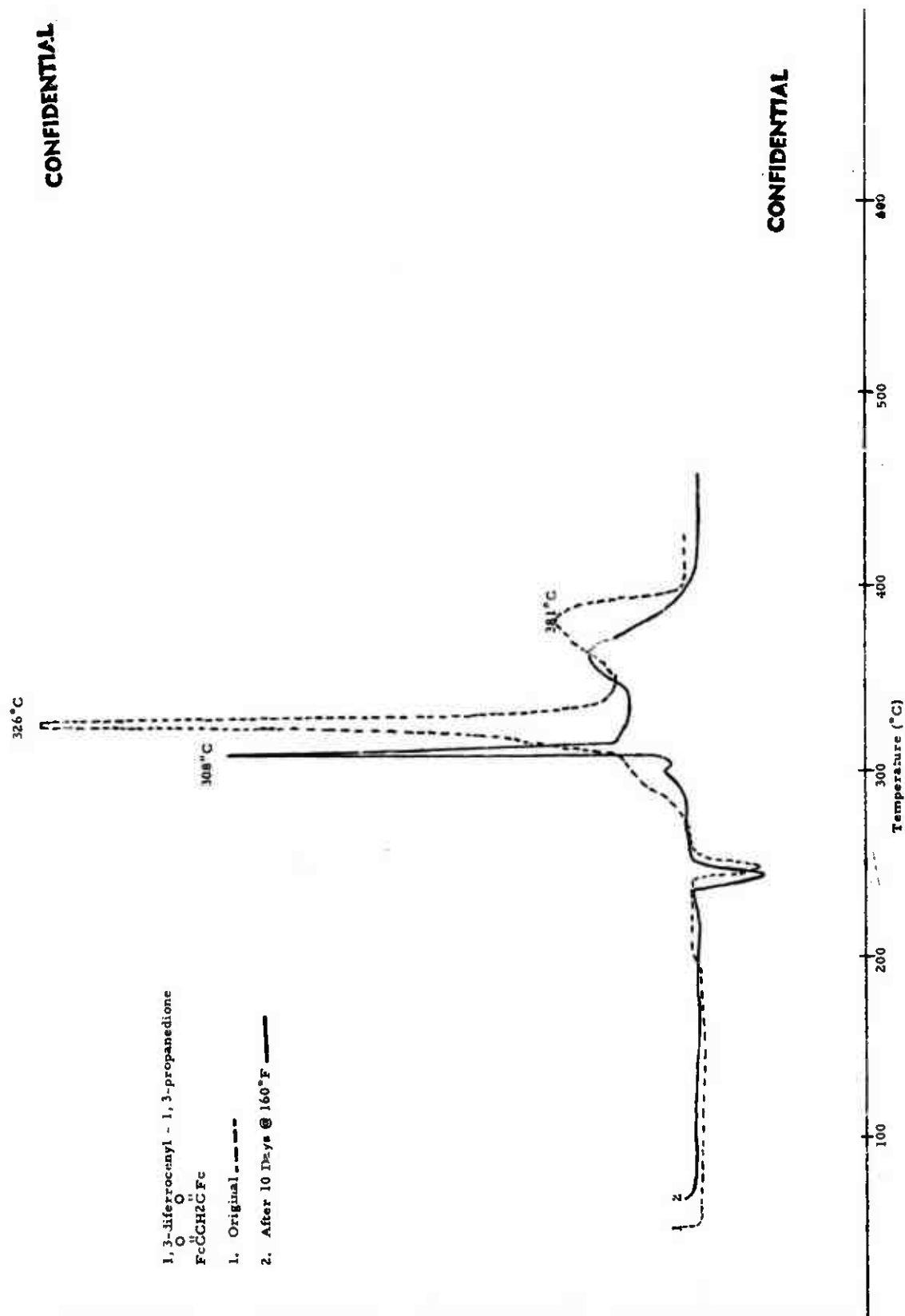
Figure 7. DTA of 1,3-diferrocenyl-1,3-propanedione.
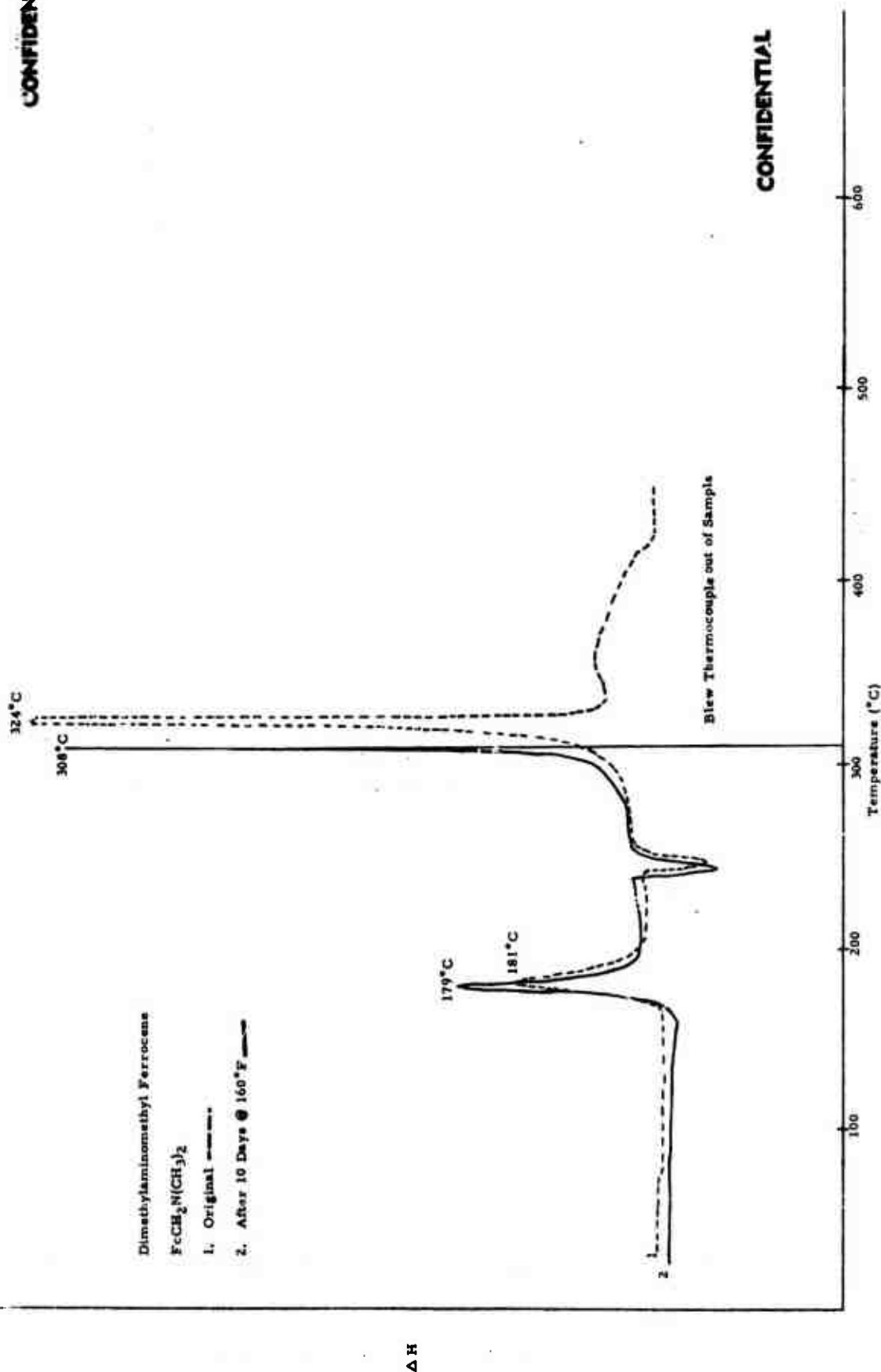
Figure 8. DTA of dimethylaminomethyl ferrocene.
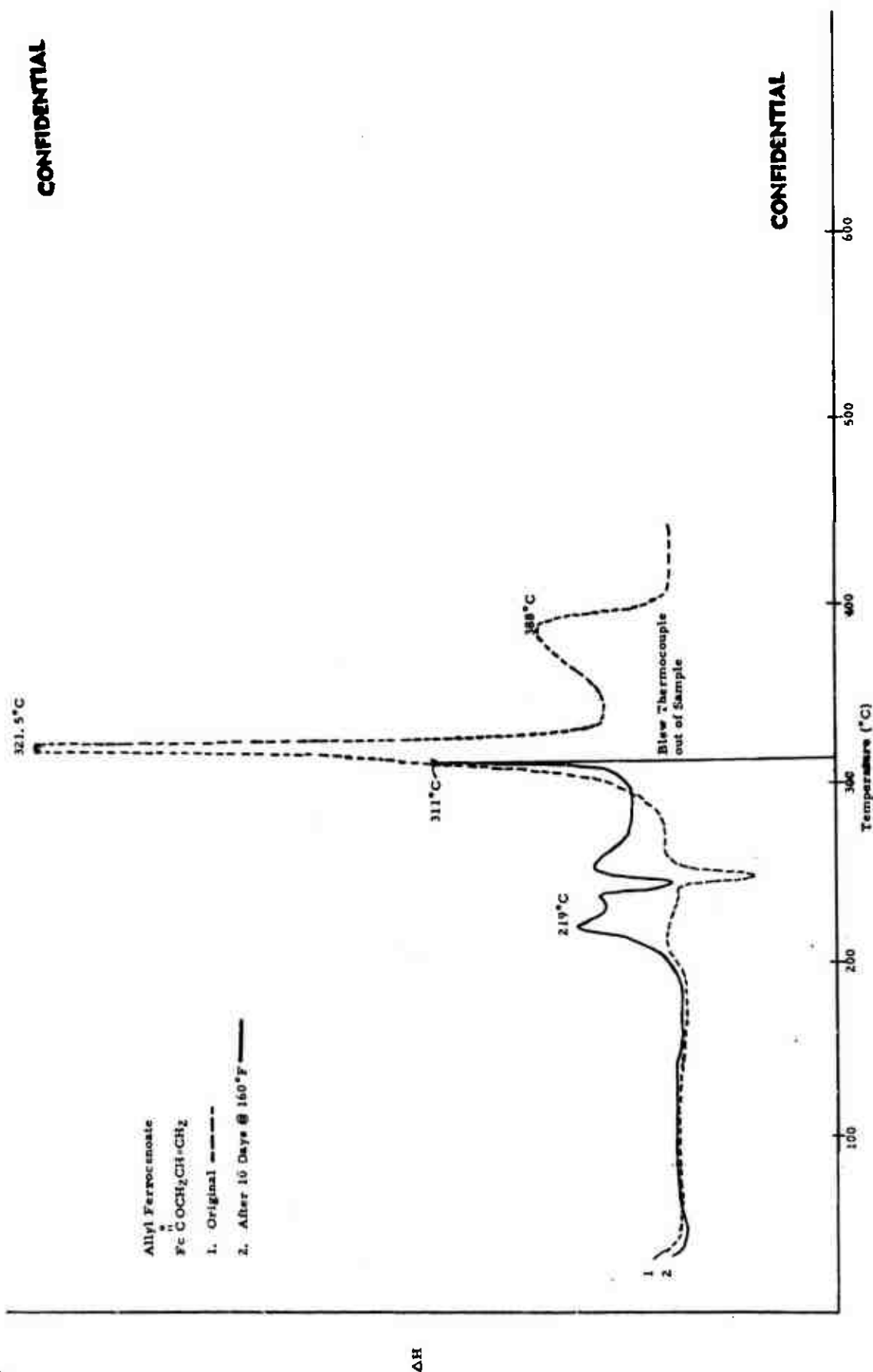
Figure 9. DTA of allyl ferrocenoate.
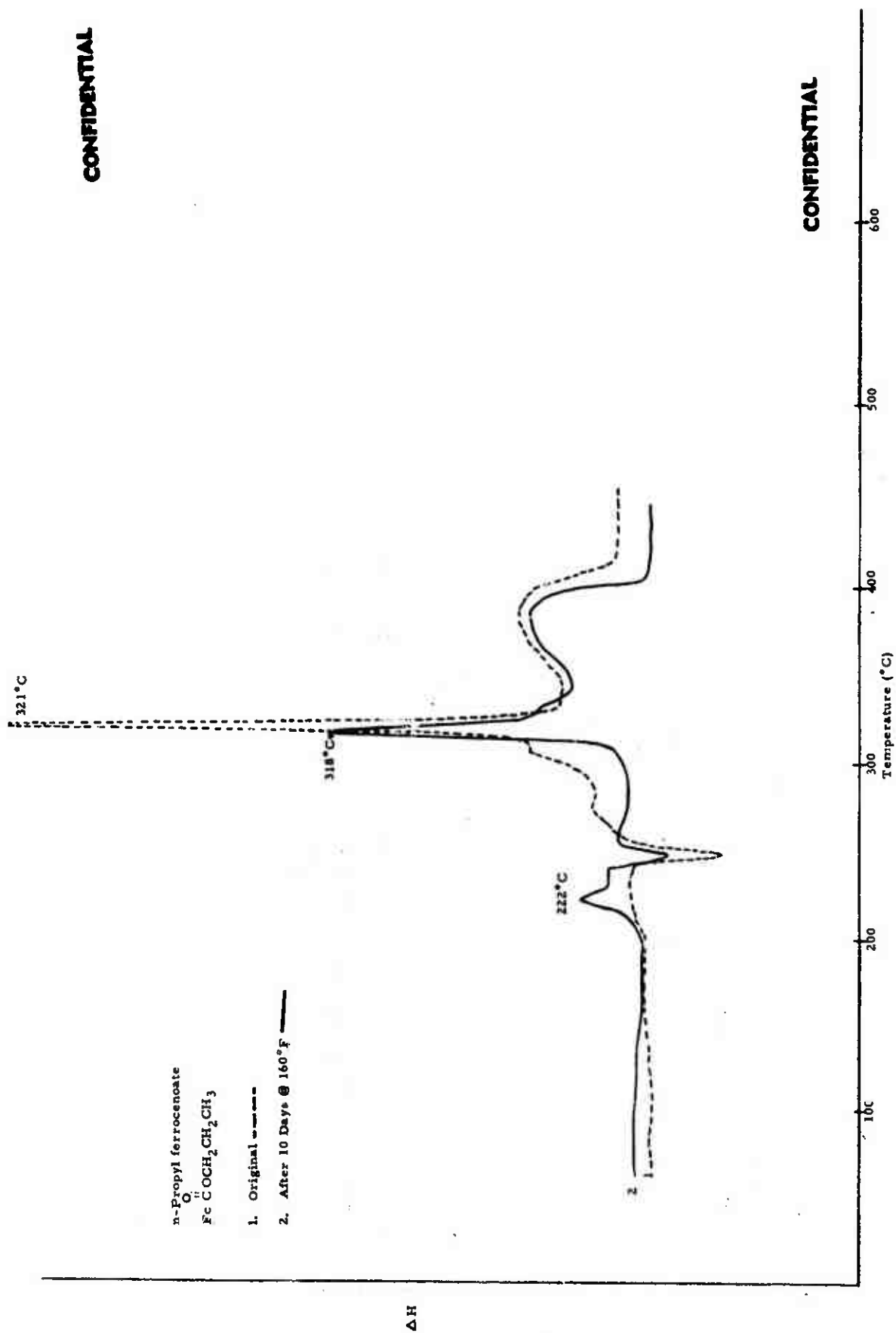
Figure 10. DTA of n-propyl ferrocenoate.
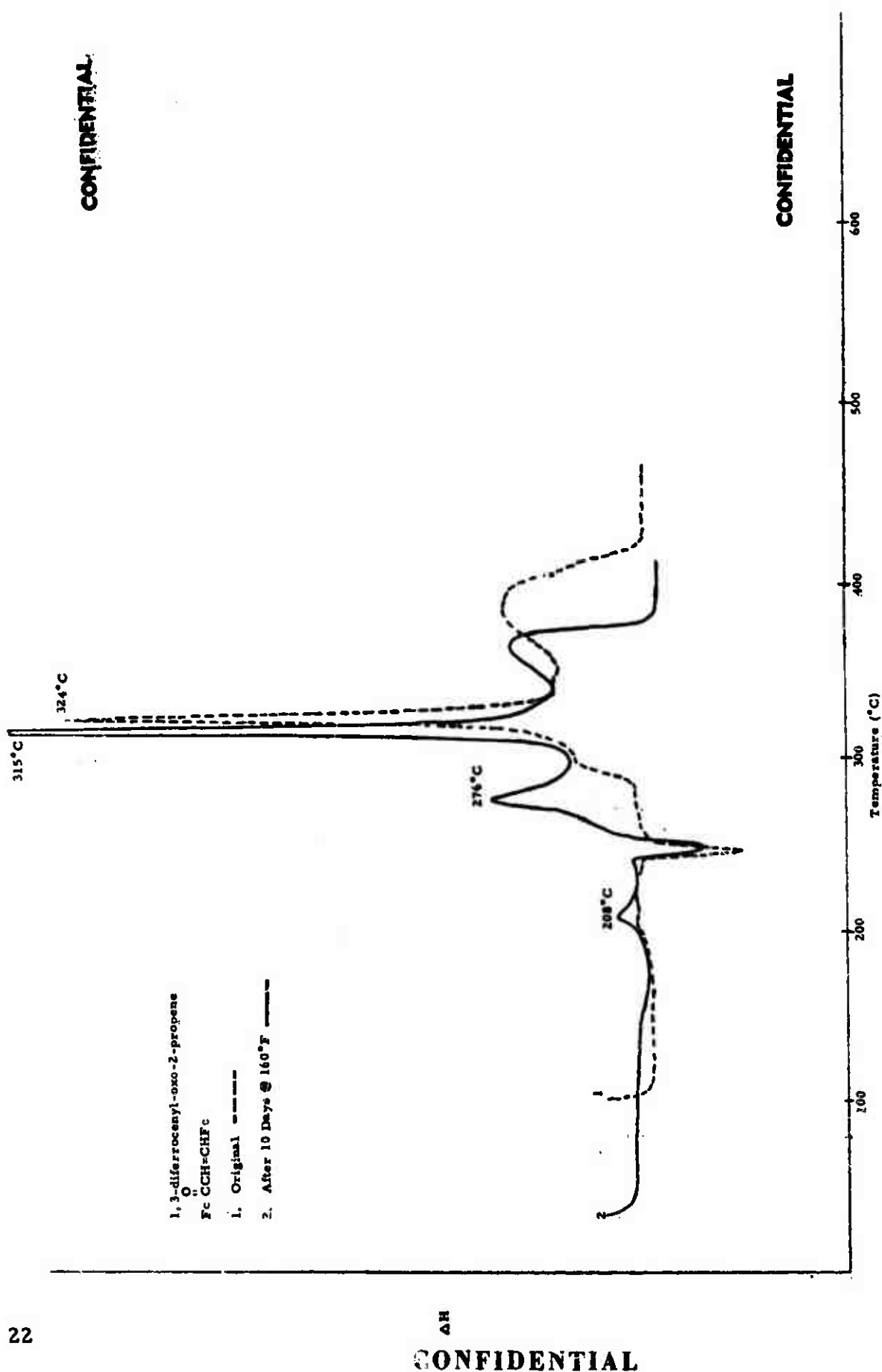
Figure 11. DTA of 1,3-diferrocenyl-oxo-2-propene.
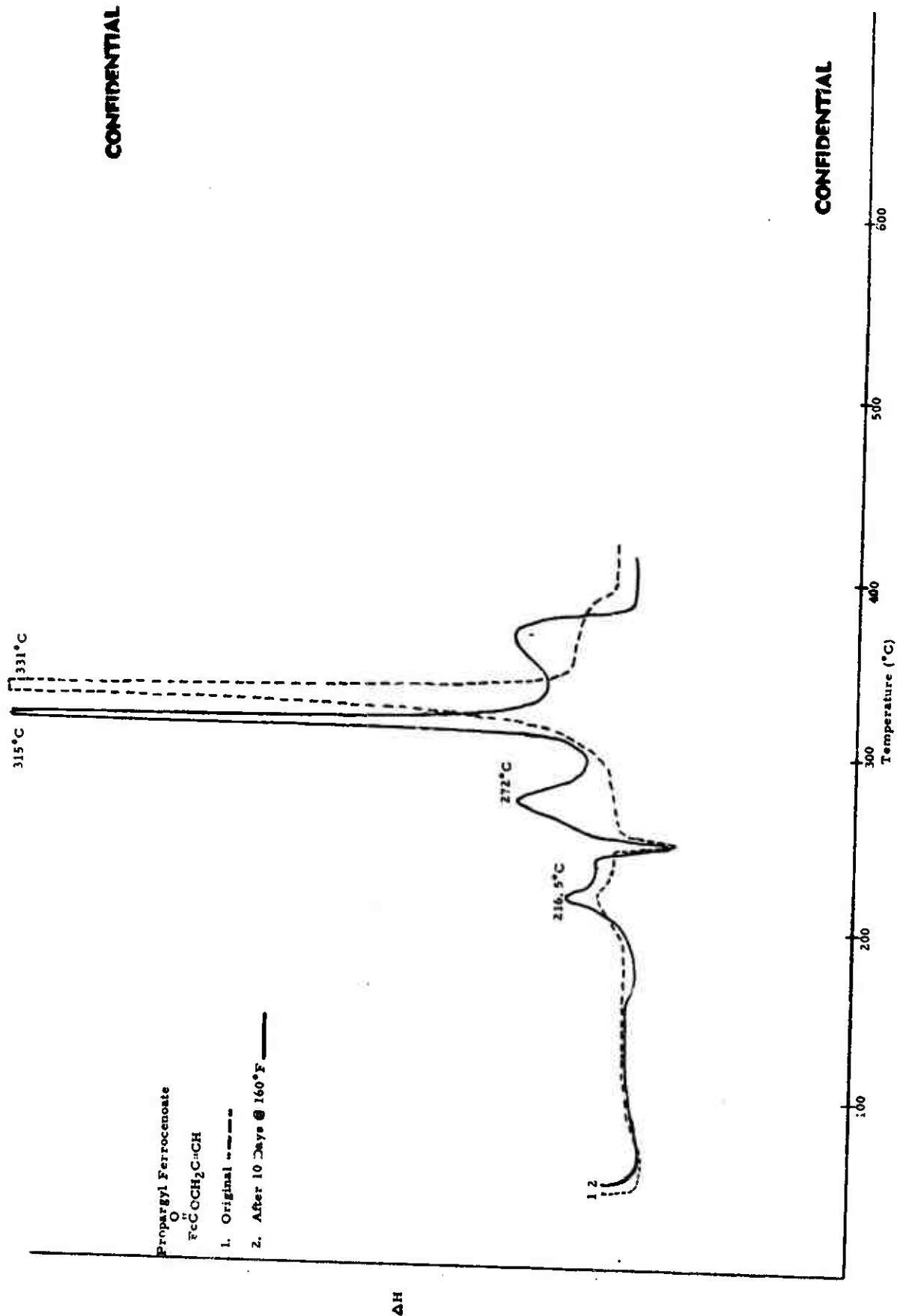
Figure 12. DTA of propargyl ferrocenoate.
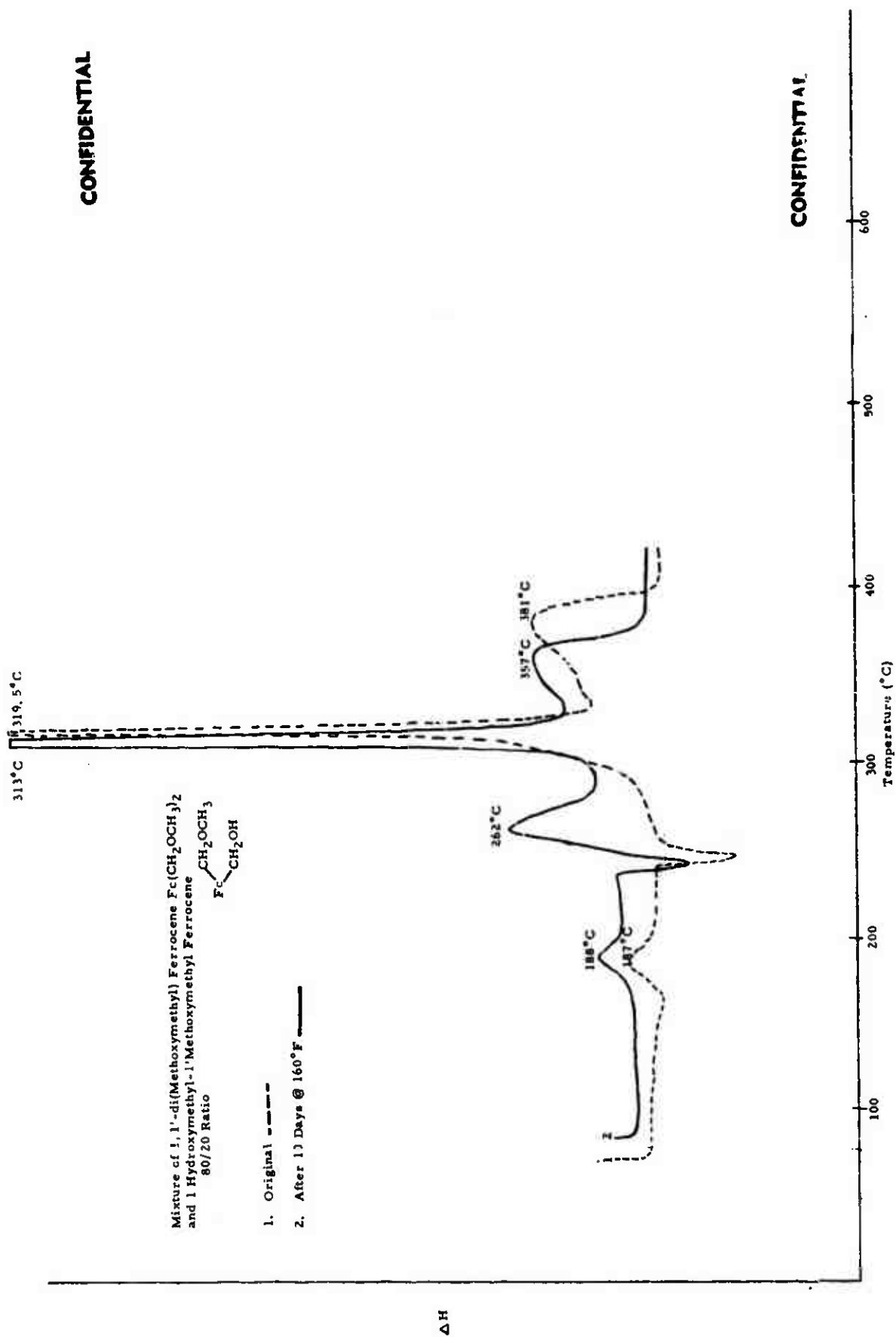
Figure 13. DTA of Mixture of 1,1'-di(methoxymethyl) ferrocene and 1 hydroxymethyl-1-1'-methoxymethyl ferrocene.

tography. The catalysts evaluated and the results of this evaluation by thin-layer chromatography (TLC) are shown in Table II. Thin-layer chromatography substantiated conclusions previously drawn that methoxymethyl ferrocene and the mixture of 1,1'-di (methoxymethyl) ferrocene with 1-hydroxymethyl-1'-methoxymethyl ferrocene also oxidized considerably. In general, TLC shows that some catalysts changed slightly, possibly because of heat or the presence of oxidizer, or both, and some trace impurities may have decomposed.

(C) Sensitivity to impact and friction was determined for a mixture of ammonium perchlorate and catalsyst (5 percent by weight) which had been aged at 160° F for 10 days. The results are summarized in Table III and are compared to non-catalyzed ammonium perchlorate and n-butyl ferrocene catalyzed oxidizer. All the catalysts compared quite favorably with n-butyl ferrocene[2] (P-IV$^{(R)}$) catalyzed oxidizer (5 percent).

(C) Some newly synthesized catalysts [methyl-β-(ferrocenylmethylthio) propionate, ferrocenylmethyl ferrocenoate, β-(ferrocenylmethylthio) ethanol] and n-butyl thiomethyl ferrocene were evaluated by DTA during this report period. These compounds do not appear to affect the decomposition of ammonium perchlorate differently than those previously tested. A plot of these data is shown on Figures 14 and 15.

(C) Figure 16 is a composite DTA plot of other recently synthesized catalysts and shows no radical difference in the decomposition of ammonium perchlorate over those catalysts evaluated previously.

(C) A tabulation of the temperatures at the major peak decomposition are as follows:

		Temperature (^{o}C)
a.	Allyloxymethyl ferrocene	320
b.	Ethoxymethylferrocene	318.5
c.	Bis-ferrocenylmethyl ether	320
d.	Methyl ferrocenylacetate	316
e.	Bis-(α-ferrocenylethyl) ether	324
f.	Ethyl ferrocenylacetate	315.5
g.	Methyl-β (ferrocenylmethylthio) propionate	326
h.	Ferrocenylmethyl ferrocenoate	320
i.	β-(ferrocenylmethylthio) ethanal	317
j.	n-butyl thiomethyl ferrocene	322

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2. U. S. Patent Secrecy Order applies.

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TABLE II

CATALYST COMPATIBILITY THIN-LAYER CHROMATOGRAPH RESULTS (160°F)

Catalyst	Original Values	Values after 10 days
$Fe(OCH_3)_3$	Spot at R_f 0, Trace at R_f 0.7	Spot at R_f 0, Trace at R_f 0.7
$Fc\ CH_2\ OCH_3$	Spot at R_f 0, Trace at R_f 0.7, 0.8, 0.9	Spot at R_f 0, R_f 0.1 - 0.2 (90%) R_f 0.2 - 0.5 (9-10%) Trace at R_f 0.5 - 0.8
$Cu^+ [Fc\ C\ CCH=CH\bar{O}]$	Spot at R_f 0, Streaked R_f 0 - 0.5, Spot R_f 0.7	Spot R_f 0, Badly streaked from R_f 0 - 0.4, Spot at R_f 0.4 (80%)
$Cu^{++} [Fc\ C\ CCH=CH\bar{O}]_2$	Streaked R_f 0 - 0.5, Trace at R_f 0.7	Spot at R_f, badly streaked from 0 - 0.5, spot at 0.5 (90%)
$Fc\ C\ OCH_2\ CH_2\ OCH_3$	Spot at R_f 0.1, 0.5, 0.7	Spot at R_f 0 (90%) trace at R_f 0.6
$Cu^{++} [Fc\ C\ CH\ CHCFc]_2$	Spot at R_f 0, R_f 0.1	Spot at R_f 0, badly streaked from R_f 0 - 0.3, Spot at R_f 0.3 (50%)
$Fc\ C\ CH_2\ C\equiv c$	Spot at R_f 0, R_f 0.2	Spot at R_f 0, dual spot at R_f 0.4 (80/10 ratio)
$Fc\ CH_2\ N(CH_3)_2$	Spot at R_f 0, R_f 0.3	Spot at R_f 0.05 (20%) and R_f 0.1 (80%) Trace at R_f 0.7
$Fc\ C\ OCH_2\ CH=CH_2$	Trace at R_f 0	Trace at R_f 0, spot at R_f 0.7
$Fc\ C\ OCH_2\ CH_2\ CH_3$	Spot at R_f 0, dual spot at R_f 0.6	Trace at R_f 0, spot at R_f 0.7
$Fc\ C\ CH = CHFc$	Trace at R_f 0, spot at R_f 0.5	Trace at R_f 0, dual spot at R_f 0.6 90/10 ratio
$Fc\ C\ OCH_2\ C=CH$	Trace at R_f 0, spot at R_f 0.5	Trace at R_f 0, spot at R_f 0.6
Mixture of $Fc\ (CH_2\ OCH_3)_2$ and $Fc\ \stackrel{CH_2\ OCH_3}{\diagup}\diagdown_{CH_2\ OH}$	Spot at R_f 0, trace at R_f 0.3, spot at R_f 0.4	Spot at R_f 0, trace at R_f 0.6

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TABLE III

IMPACT AND FRICTION SENSITIVITY OF CATALYST/AMMONIUM PERCHLORATE(5%)

Catalyst	F_o (rpm)	E_o (Kg-cm)
Trimethoxy Iron	>6000	100 +
Methoxymethyl ferrocene	>6000	50
Copper (I) complex of β-ferrocenyl-β-oxo-propionaldehyde	>6000	70
Copper (II) complex of β-ferrocenyl-β-oxo-propionaldehyde	>6000	100 +
2-Methoxyethyl ferrocenoate	>6000	100 +
Copper complex of 1, 3, -diferrocenyl-1, 3-propanedione	>6000	100 +
1, 3-diferrocenyl-1, 3-propanedione	>6000	100 +
Dimethylaminomethyl ferrocene	>6000	60
Allyl ferrocenoate	>6000	70
n-propyl ferrocenoate	>6000	70
1, 3-diferrocenyl-1 oxo-2 propene	>4000	100 +
Propargyl ferrocenoate	>6000	100 +
Mixture of 1, 1'-di(methoxymethyl) ferrocene and 1 hydroxymethyl-1'-methoxymethyl ferrocene	>6000	70
$Fc(CH_2OCH_3)_2$ & $Fc \begin{smallmatrix} CH_2OCH_3 \\ CH_2OH \end{smallmatrix}$		
Ammonium perchlorate	>6000	100 +
n-butyl ferrocene [PLASTISCAT-IV (R)]	>6000	50

1. FcCH$_2$SCH$_2$CH$_2$CO$_2$CH$_3$ - Methyl-β-(ferrocenylmethylthio) propionate
2. FcCO$_2$CH$_2$Fc - Ferrocenylmethyl ferrocenoate
3. FcCH$_2$SCH$_2$CH$_2$OH - β-(ferrocenylmethylthio) ethanol
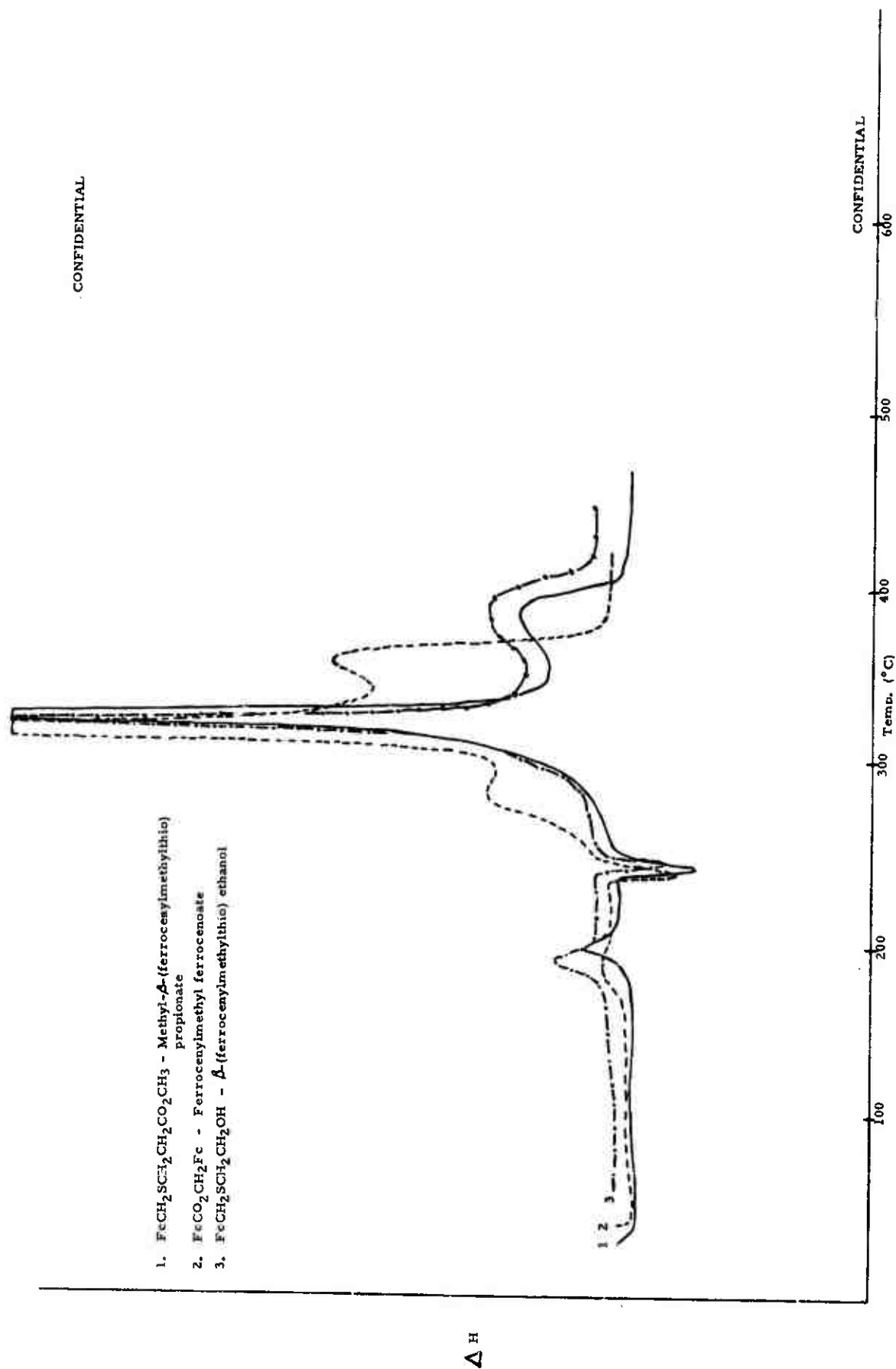
Figure 14. Differential Thermal Analyses of methyl-β-(ferrocenylmethylthio) propionate, ferrocenylmethyl ferrocenoate, and β-(ferrocenylmethylthio) ethanol.

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FcCH$_2$SCH$_2$CH$_2$CH$_2$CH$_3$
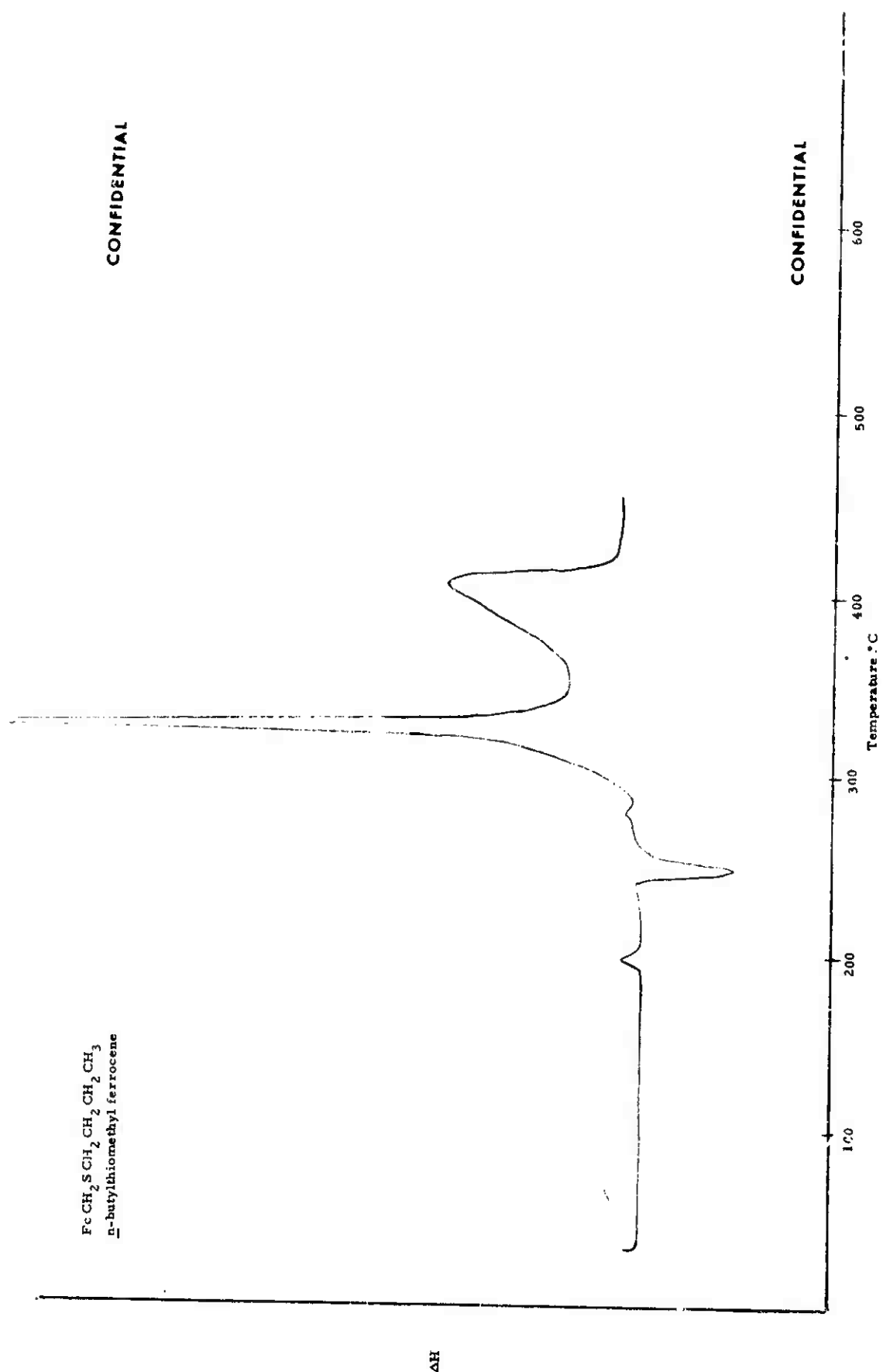n-butylthiomethyl ferrocene

ΔH

Temperature °C

Figure 15. Differential Thermal Analysis of Ammonium Perchlorate (ung) + 5% Catalyst.

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Figure 16. DTA of 5 Percent Catalyst with AP

(U) Figures 17, 18 and 19, show percent weight loss by TGA method of:

  a. Copper (II) complex of β-ferrocenyl- β-oxo-propionaldehyde.
  b. Dimethylaminomethyl ferrocene.
  c. 1,3-diferrocenyl-1 oxo-2-propene.

(C) Visual observations show that ethyl ferrocenylacetate (which contains one percent t-butylhydroquinone) oxidizes rapidly at room temperature when exposed to the atmosphere and oxidizes slightly when sealed. Also, n-butyl thiomethyl ferrocene shows slight oxidation at room temperature after several weeks.

(U)   b. Burn Rate Studies

(C) A 1000 gram batch of HC propellant without burning rate catalyst and curing agent was made and 100 gram batches of propellant containing rate catalyst and curing agent were prepared from the master batch. Composition of the propellant used is shown below:

Composition	Weight, %
HC Binder	13.30
MAPO	0.70
AP (unground)	27.20
AP (9600)	40.80
Al (H-5)	16.00
Catalyst	2.00

(C) Propellant mixes containing methoxymethyl ferrocene and n-butyl ferrocene [P-IV$^{(R)}$], in concentrations of two percent, were prepared and evaluated for a comparison of burning rates. The evaluation was conducted in the pressure range of 400 - 1200 psig and the propellants were burned as strands. The data obtained (Figure 20) indicates that methoxymethyl ferrocene yields an increase in burning rate and displays a lower pressure exponent.

(C) Addition of dimethylaminomethyl ferrocene to the mix (rate catalyst added last in all cases) caused immediate release of ammonia gas, which was noted until the end of vacuum mixing (25 minutes after addition of the catalyst). Several explanations can be offered as to why ammonia gas evolved:

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Figure 17. Percent Weight Loss versus Temperature by TGA Method -- Copper (II) Complex β-ferrocenyl-β-oxo-propionaldehyde $[Cu^{++}(Fc\overset{O}{\underset{\parallel}{C}}CH = CHO^-)_2]$

32
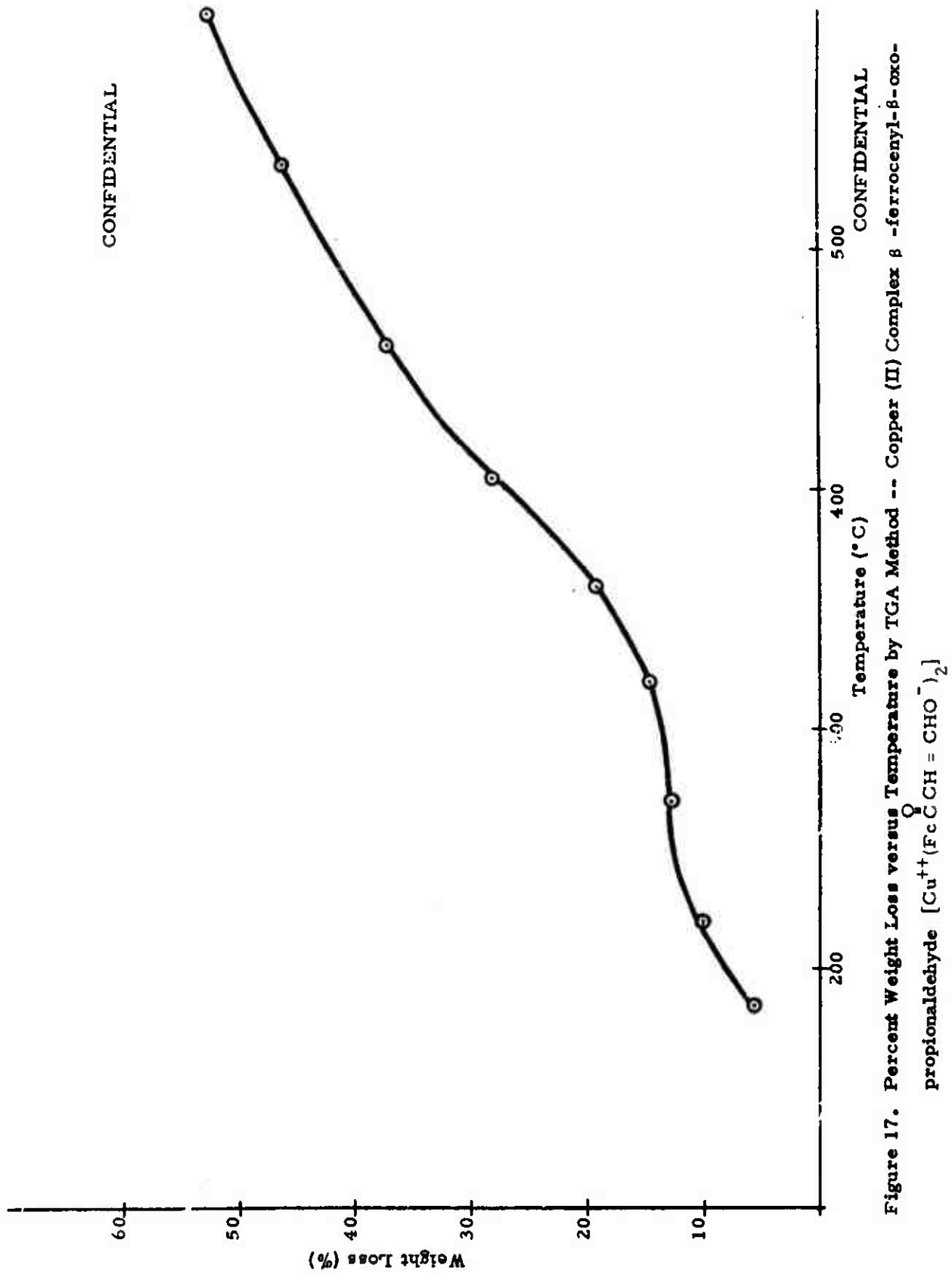
Figure 18. Percent Weight Loss versus Temperature by TGA Method - dimethylaminomethyl ferrocene $[Fc\,CH_2\,N\,(CH_3)_2]$
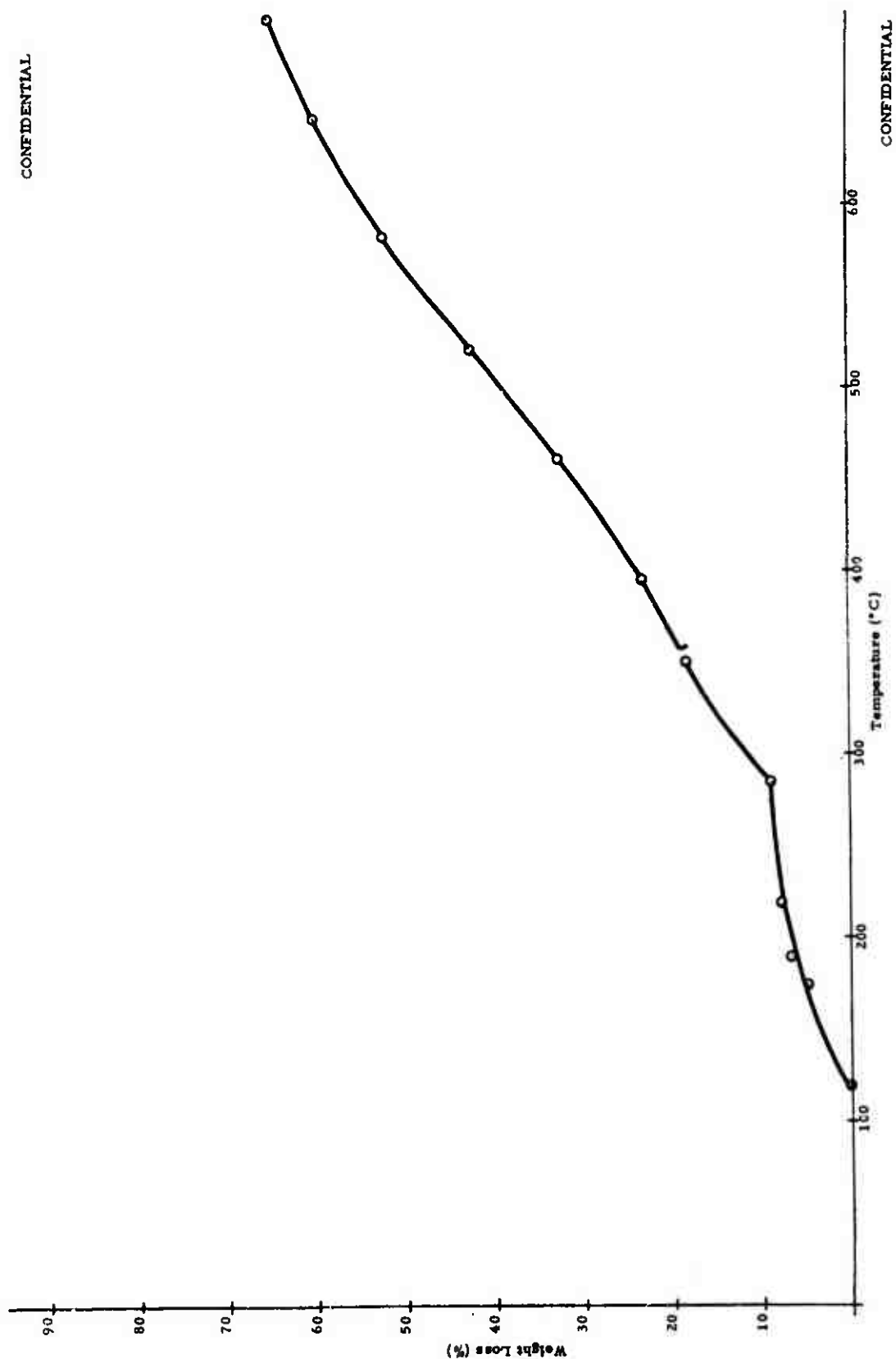
Figure 19. Percent Weight Loss versus Temperature by TGA Method -- 1,3-diferrocenyl-1 oxo-2-propene (Fc CH = CH C Fc)
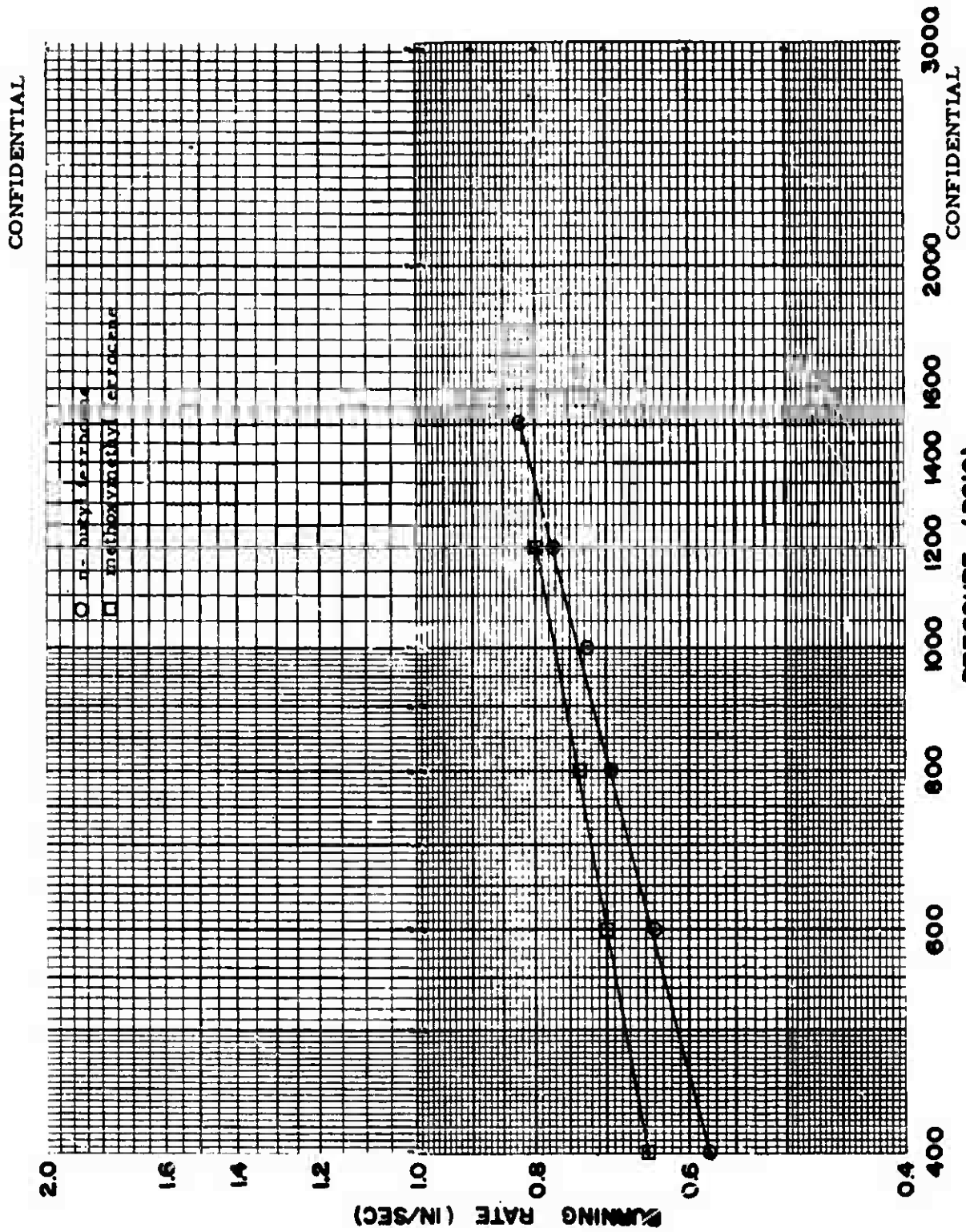
Figure 20. Comparison of the Burning Rate Characteristics of Propellants Catalyzed with PLASTISCAT-IV(X) and Methoxymethyl Ferrocene.

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1. dimethylaminomethyl ferrocene reacted with ammonium perchlorate.
2. dimethylaminomethyl ferrocene decomposed
3. dimethylaminomethyl ferrocene reacted with MAPO

The latter explanation would appear to be the most plausible since the propellant failed to cure in 7 days at 135° F. Consequently, no data are available as yet to show the burning rate potential of this material.

(U) Other catalysts evaluated were:

> 1, 3-diferrocenyl-1 oxo-2 propene
> bis (α -ferrocenylethyl) ether
> alloxymethyl ferrocene
> ethoxymethyl ferrocene

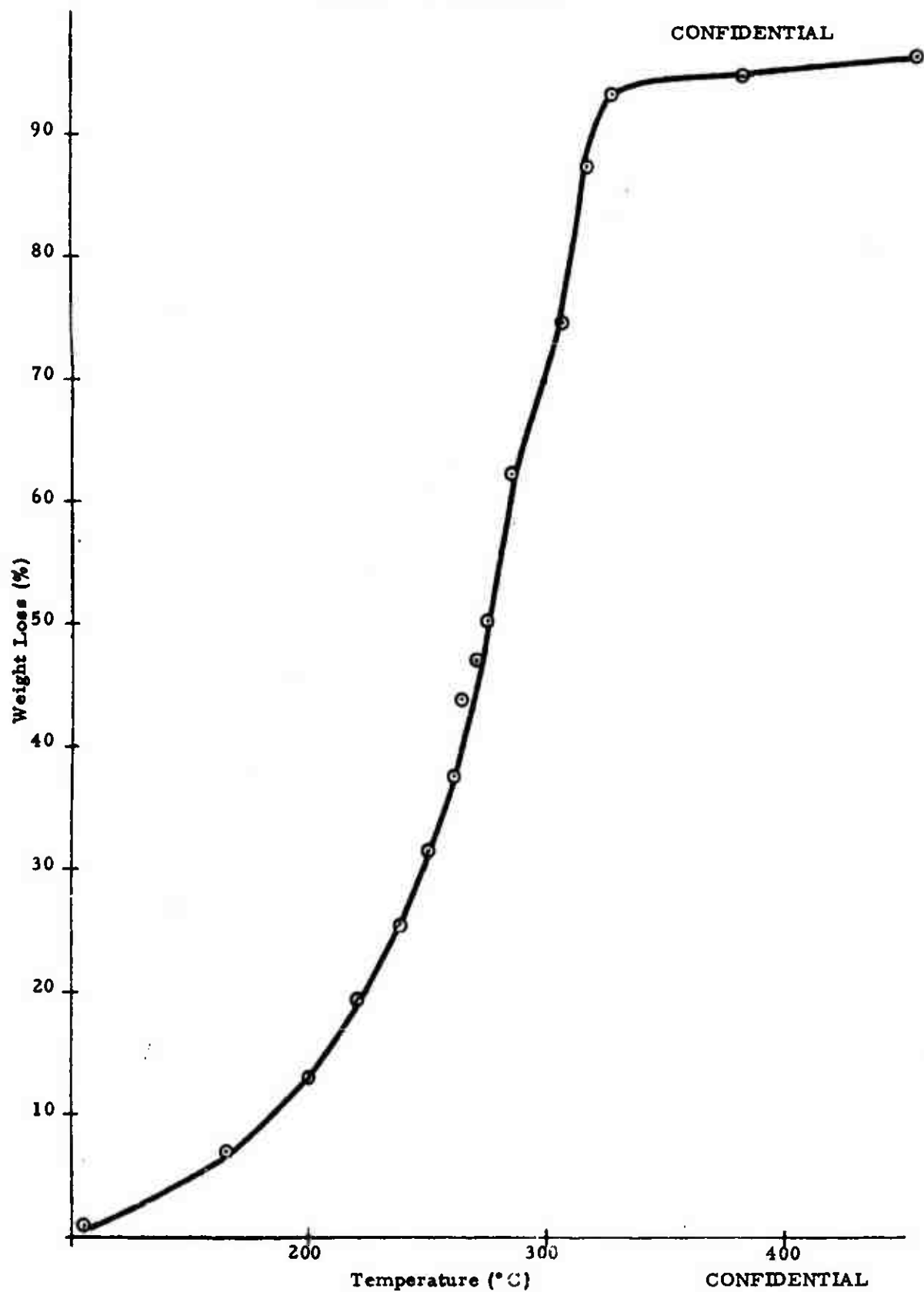(C) The burning rates of propellant containing the catalysts evaluated are illustrated on Figure 21. These data show that although 1, 3-diferrocenyl-1 oxo-2 propene did not disperse well, the burning rate of propellant containing this catalyst is considerably better than that of the propellant containing n-butyl ferrocene [PLASTISCAT-IV$^{(R)}$]. Propellants containing methoxymethyl ferrocene and bis (α -ferrocenylethyl) ether also demonstrated a higher burning rate than propellant containing n-butyl ferrocene. As predicted, bis (α -ferrocenylethyl) ether, alloxymethyl ferrocene and ethoxymethyl ferrocene lowered the propellant viscosity to the 20 to 25 Kp. range. Observations concerning the mechanical properties and sensitivity of these formulations are tabulated in Table IV.

(U) The burn rate characterization of a further series of catalysts has been accomplished. The catalysts evaluated were:

> methyl ferrocenylacetate
> ethyl ferrocenylacetate
> methyl β - (ferrocenylmethylthio) propionate
> poly- [bis (methylthiomethyl) ferrocene]

(C) Characteristics of the cured propellants are summarized in Table V. During cure, a tough, leathery "skin" formed on the surface of each of the propellants containing methyl ferrocenylacetate and ethyl ferrocenylacetate. A skin was also observed on the surface of samples of these propellants, which had been removed from the mixer and allowed to cool to ambient temperature. In the latter case, the skin was not as thick or tough as that on the cured propellant.

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TABLE IV

PHYSICAL PROPERTY CHARACTERISTICS AND SENSITIVITY TEST RESULTS OF CATALYZED PROPELLANT

Catalyst	SHORE "A" DURO	Cure Time (hrs)	Physical Property	Friction Sensitivity (rpm)	Impact Sensitivity (E_o) (kg-cm)
1,3-diferrocenyl-1 oxo-2 propene	50	48	good	5000 +	54
bis (α -ferrocenylethyl) ether	45	48	slightly plastic	5000 +	155
alloxymethyl ferrocene	45	48	slightly plastic	5000 +	150
ethoxymethyl ferrocene	55	72	high modulus	5000 +	125
dimethylaminomethyl ferrocene	Did not cure			5000 +	98

TABLE V

CHARACTERISTICS OF CATALYZED PROPELLANT

Catalyst	Shore "A" DURO	Cure Time	Physical Properties
Methyl ferrocenylacetate	52	44	Good. Forms tough "skin" on top during cure.
Ethyl ferrocenylacetate	46	68	Low modulus, slightly plastic.
Methyl β-(ferrocenylmethylthio) propionate	34	68	Very low modulus.
Poly-[bis(methylthiomethyl) ferrocene]	53	40	Good.
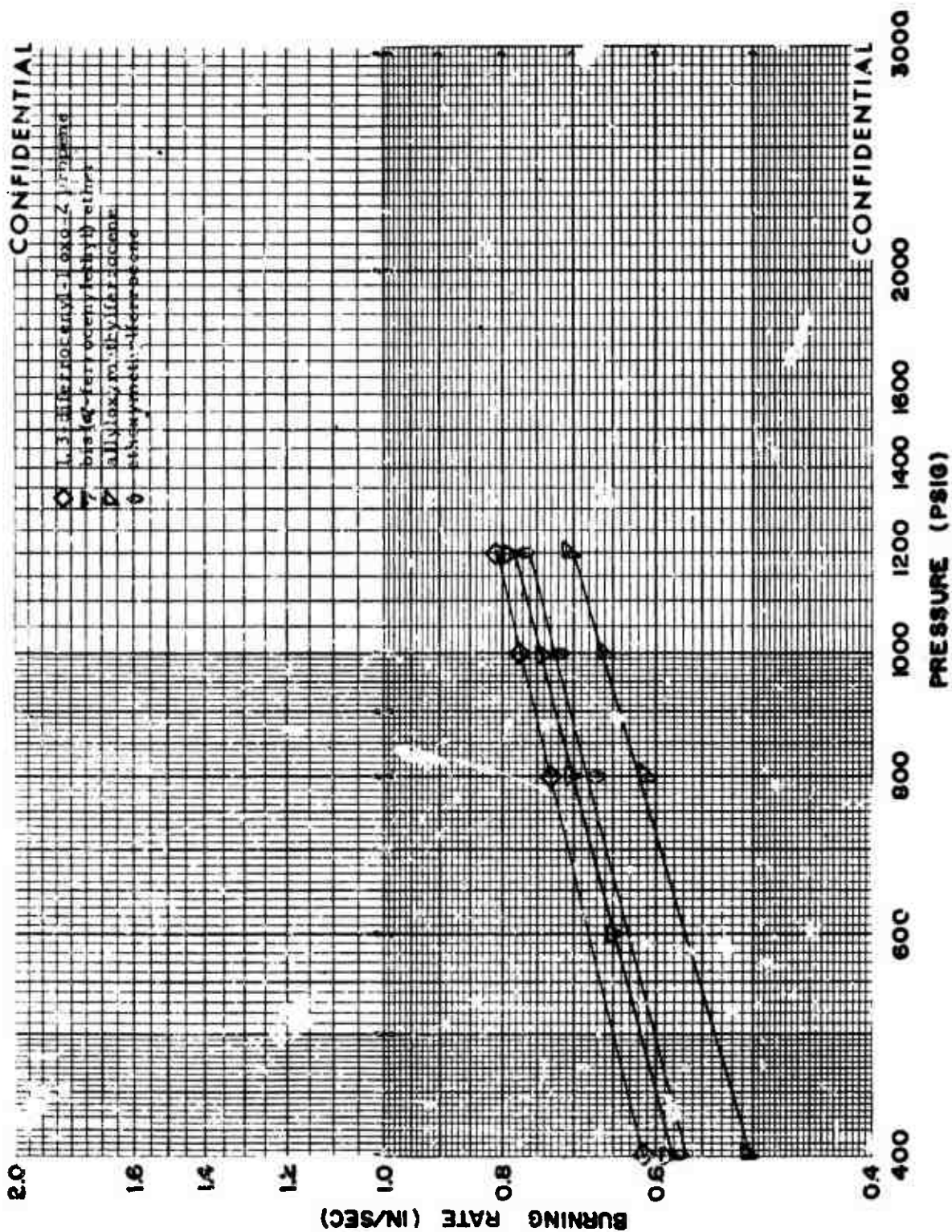
Figure 21. Comparison of the Burning Rate Characteristics of Propellants Catalyzed with 1, 3-diferrocenyl-1-oxo-2 propene, bis (α-ferrocenylethyl) ether, allyloxymethyl ferrocene and ethoxymethyl ferrocene.

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(C) Addition of methyl ferrocenylacetate and ethyl ferrocenylacetate to the mixer caused a significant drop in viscosity of each propellant to the 15 to 20 kilopoise range. Addition of methyl β-(ferrocenylmethylthio) propionate to the propellant mix effected a viscosity reduction to the 20 to 25 kilopoise range. No reduction in viscosity was experienced with the addition of mercaptomethyl terminated poly -[bis (methylthiomethyl) ferrocene].

(C) A comparison of the characteristics of the catalyzed propellants can be made with that of n-butyl ferrocene on Figures 20, 22 and 23. These data show the burning rate characteristics for ethyl ferrocenylacetate to be slightly higher than that of n-butyl ferrocene, while the burning rate of methyl ferrocenylacetate is equal to that of n-butyl ferrocene. A propellant mix containing copper (II) complex of β- ferrocenyl- β -oxo-propionaldehyde was still in cure at the end of this report period. Data from this mix will be reported in a subsequent report.
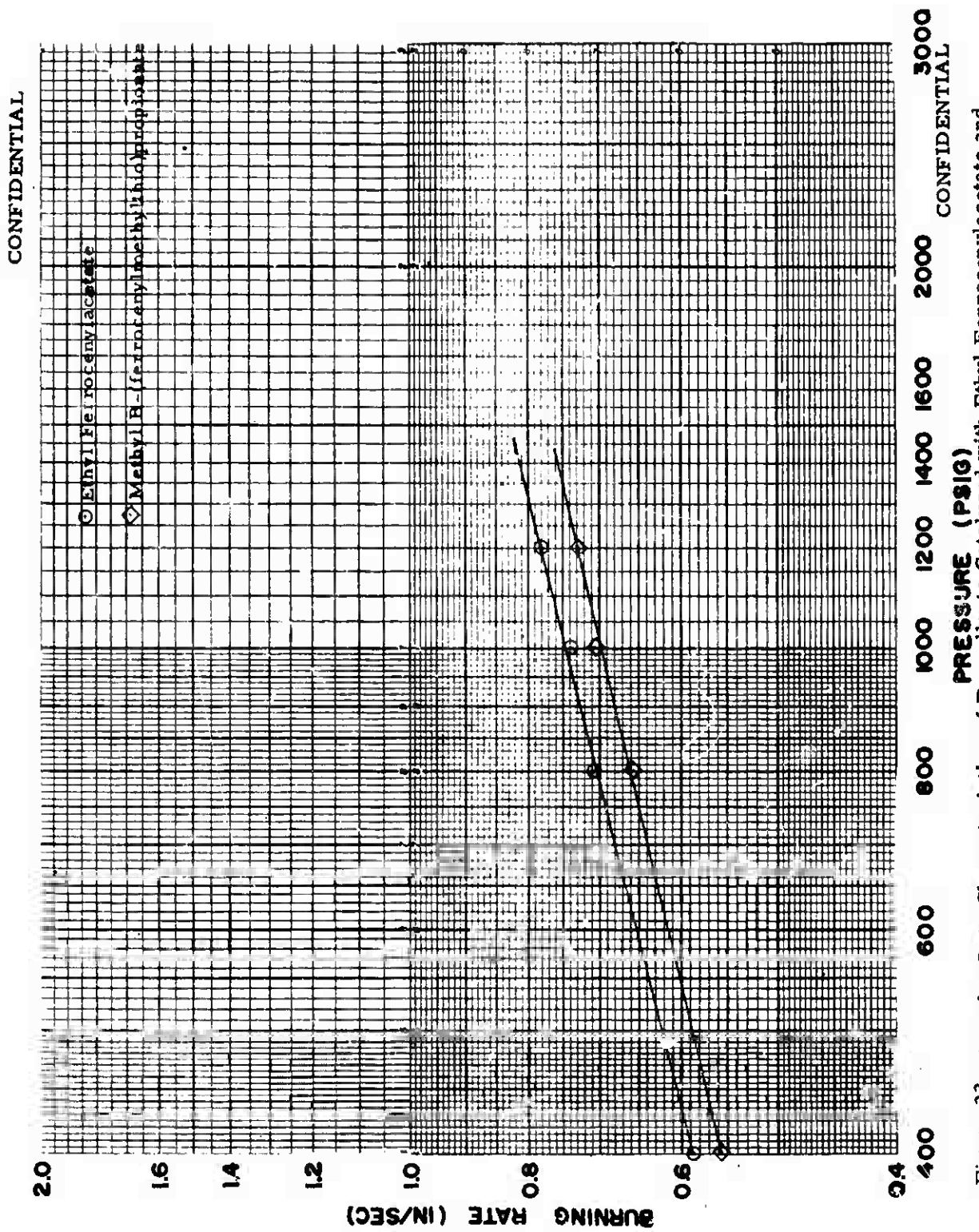
Figure 22. Burning Rate Characteristics of Propellants Catalyzed with Ethyl Ferrocenylacetate and Methyl-β-(ferrocenylmethylthio)propionate.

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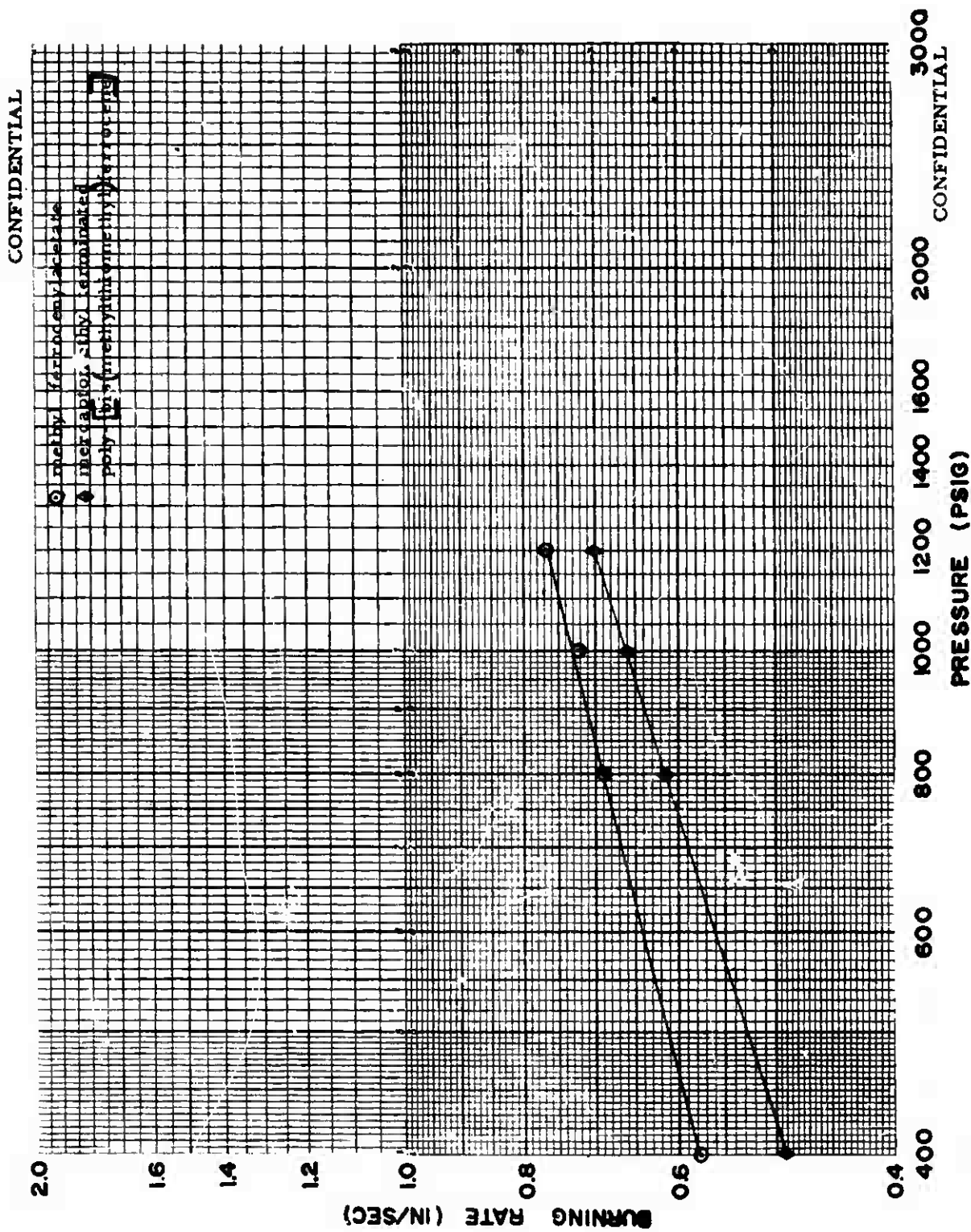
Figure 23. Burning Rate Characteristics of Propellants Catalyzed with Methyl Ferrocenylacetate and Mercaptomethyl Terminated poly-[bis(methylthiomethyl) ferrocene].

SECTION III

CONCLUSIONS

1. (U) Thirty candidate catalyst materials have been synthesized and the physical properties ascertained.

2. (C) The previously reported freezing points of the candidate catalysts have been found to be in error due to extreme degrees of supercooling which seem to be characteristic of liquid ferrocene derivatives. Melting points, which are not as time dependent as freezing points, will be reported in the future.

3. (U) Compatibility testing of the catalyst materials with oxidizer, curing agents, etc., are essentially complete and, with the exception of dimethylaminomethyl ferrocene, no serious problems are expected in the formulation and scale-up of propellants containing the candidate catalysts.

4. (C) Burn rate studies thus far indicate that several prospective liquid ferrocene derivatives offer considerable potential in increasing burn rates over that presently available with n-butyl ferrocene [PLASTISCAT-IV[R]].

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	2b. GROUP IV

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11. SUPPLEMENTARY NOTES ---	12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Division Edwards Air Force Base, California 93523

13. ABSTRACT (C) Thiokol's program to tailor the burning rate of a propellant predictably and controllably to any desired level in the range from one to ten inches per second is divided into three phases: Phase I-Synthesis of Burning Rate Catalysts, Phase II-Decomposition Studies and Evaluation of Catalysts and Phase III-Decomposition of Advanced Oxidizers, Fuels, and Binders. Experiments will be performed to synthesize more efficient burn rate catalysts by maximizing already determined guideline properties toward development of an ideal catalyst under Phases I and II. Following catalyst synthesis, each compound showing potential will be subjected to comprehensive decomposition studies and combustion mechanism evaluation with propellant ingredients. To date, 30 candidate catalysts materials have been synthesized and the physical properties ascertained. Compatibility testing of these materials is essentially complete and no serious problems are expected in the formulation and scale-up of propellants containing the candidate catalysts. Burn rate studies thus far indicate that several prospective liquid ferrocene derivatives offer considerable potential in increasing burn rates over that presently available with n-butyl ferrocene [PLASTISCAT-IV$^{(R)}$].

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14 KEY WORDS	LINK A		LINK B		LINK C	
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Combustion mechanism						
Burn rate						
Catalyst synthesis						
Decomposition studies						

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There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

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