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**OXIDATION-RESISTANT METALLOCENES.
THE THERMAL AND OXIDATIVE STABILITY
OF POLYCHLORINATED METALLOCENES**

*FREDERICK L. HEDBERG
HAROLD ROSENBERG*

TECHNICAL REPORT AFML-TR-71-267

MARCH 1972

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was conducted under Project 7342, "Fundamental Research on Macromolecular Materials," Task 734201, "Basic Factors in the Synthesis of Macromolecular Materials." It was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (AFML/LNP) as Project Scientist.

This report covers research conducted from May 1969 to October 1970. It was submitted by the authors in March 1971.

This technical report has been reviewed and is approved.



R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

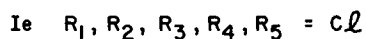
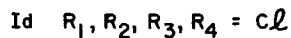
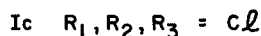
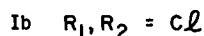
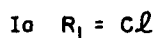
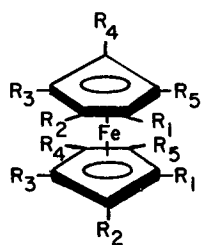
Polychlorinated metallocenes, including the recently synthesized decachloroferrocene and decachlororuthenocene, were investigated to determine the effect of increasing number of electron-withdrawing substituents on the thermal and oxidative stability of such metallocenes. Thermal analysis, including use of differential scanning calorimetry, indicated a definite, although not drastic, decrease in thermal stability with increasing chlorine content in these systems. Much greater (thermal) stability, as well as enhanced oxidative stability, was evidenced for decachlororuthenocene than for decachloroferrocene. In connection with the thermal analytical investigation, mesophases were discovered in 1, 1', 2, 2'-tetrachloroferrocene, 1, 1', 2, 2', 3, 3', 4, 4'-octachloroferrocene and decachlororuthenocene, some of which appeared to be liquid crystalline in nature.

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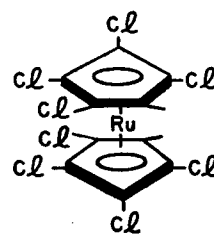
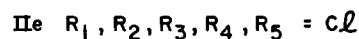
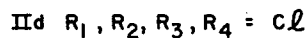
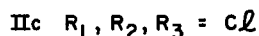
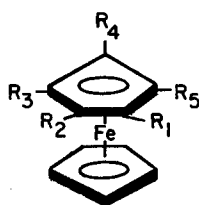
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SECTION I
INTRODUCTION

The recently reported (Reference 1) synthesis of decachloroferrocene (Ie), decachlororuthenocene (III) and the related polychlorinated compounds (Ib-Id and IIb-IIe) affords an opportunity for investigating the effect of increasing numbers of electron-withdrawing substituents on the thermal and oxidative properties of metallocenes.



($R_n = H$ Unless Otherwise Indicated)



III

Two deca-substituted derivatives of ferrocene have previously been reported, decaethylferrocene (Reference 2) and decamethylferrocene (References 3 and 4). Only the latter compound was fully characterized, with melting points of 277-278° (Reference 3) and 291-295° (Reference 4) reported. There thus appears to be no pronounced destabilizing steric effect from having 10 methyl groups on ferrocene. Since methyl and chlorine groups can be considered as roughly the

same size, there would appear to be no steric reason for Ie to be thermally unstable. This reasoning should also be applicable to III, with the greater distance between the rings further diminishing inter-ring chlorine interactions.

The analogy between methyl and chlorine groups on ferrocene breaks down, however, when inductive effects are considered. The electron withdrawal caused by 10 chlorines might be expected to have a severe weakening effect on either the Fe-ring bonding in Ie or the Ru-ring bonding in IIIa. The much greater ease of oxidation shown by decamethylferrocene versus ferrocene itself may similarly be attributed to the electron donating characteristic of the methyl group, since electron donors are known to decrease the oxidation potential of ferrocene (References 5, 6, and 7).

Electron-withdrawing substituents, on the other hand, have been shown to increase the oxidation potential of ferrocene in an additive manner, both for heteroannular (Reference 6) and homoannular (Reference 7) substitution. Chloroferrocene was found (Reference 5) to oxidize at a potential 0.163 volts higher than ferrocene, while 1,1'-dichloroferrocene was found (Reference 6) to oxidize 0.309 volts higher than ferrocene. Multiplying the latter figure by 5 gives a value of approximately 1.5 volts for the predicted increase in oxidation potential of decachloroferrocene versus ferrocene. Such an extrapolation from 2 to 10 chlorines is obviously tenuous. It is interesting, however, to compare the calculated potential difference for decamethylferrocene versus ferrocene of -0.47 volts (10 times the oxidation potential differential between methylferrocene and ferrocene (Reference 5) with the reported value of -0.43 volts (Reference 3).

SECTION II

DISCUSSION AND EXPERIMENTAL

That these homoannular and heteroannular additive effects are at least qualitatively applicable to the series of chlorinated ferrocenes was shown by reactions with concentrated nitric acid at 23°. Ferrocene, 1,1'-dichloroferrocene and 1,1, '2, 2'-tetrachloroferrocene were oxidized immediately upon contact, giving first the blue color of the corresponding ferrocenium ions, which faded quickly to yellow presumably upon degradation to ferric ion. 1,1',2,2', 3,3'-hexachloroferrocene was oxidized within one minute directly to a yellow solution, the rate constant for degradation of the intermediate ferrocenium ion apparently being much larger than the rate constant for its formation. Both 1,1',2,2',3,3',4,4'-octachloroferrocene and decachloroferrocene were undissolved after 10 minutes at 100° in concentrated nitric acid. To differentiate the relative oxidation stabilities of these last two members of the series, a carbon tetrachloride solution of each compound was stirred vigorously with concentrated nitric acid at 23° for 29 hours. The octachloroferrocene was destroyed, while the decachloroferrocene was recovered unchanged. This technique was also applied on a preparative basis for purification of decachloroferrocene.

One significant implication of the high oxidative stability of the highly chlorinated ferrocenes is that reactions or studies in strong oxidizing environments, impossible with ordinary ferrocene derivatives, may be carried out with these novel ferrocenes. The enhanced oxidation stability displayed by the higher chlorinated ferrocenes might also be attributed to steric protection of the iron atom by the chlorine atoms. That such an explanation is not valid is shown by the fact that decamethylferrocene, as mentioned above, shows the predicted decrease in oxidation potential, since methyl and chlorine groups can be considered as sterically equivalent.

Decachlororuthenocene was dissolved in carbon tetrachloride and stirred at 23° with concentrated nitric acid. The material was recovered unchanged after 68 hours, demonstrating an enhancement in oxidation stability for the ruthenocene system (ruthenocene itself is oxidized immediately by concentrated nitric acid) analogous to that obtained for the ferrocene system.

The melting and decomposition points of the unsymmetrically chlorinated derivatives IIb-IIe were determined in sealed capillary tubes under nitrogen and are given in Table I. The decomposition points show a downward trend with increasing chlorine content, in accord with the expected destabilizing effect of these electron-withdrawing substituents.

A more thorough study of the thermal behavior of the symmetrically chlorinated derivatives Ia-Ie and III was carried out by means of differential scanning calorimetry. The results are shown in Table II. A downward trend in decomposition temperatures with increasing chlorine content is noticeable for Ia-Id. The decomposition of Ie occurs from the solid state and therefore cannot be correlated with the liquid state decomposition occurring with Ia-Id. The significantly higher decomposition of III versus that of Ie, however, can be interpreted as demonstrating much greater thermal stability for the perchlorinated ruthenocene system over that of the perchlorinated ferrocene system.

Some interesting anomalies can be seen from the data in Table II. Ic shows a second decomposition exotherm, indicating some sort of discrete, two-step decomposition for this compound. Compounds Ib, Id, and IIIa each have two endotherms below the melting endotherm which, upon visual observation under a hot stage microscope, appear to be transitions to a mesophase whose nature appears to be that of either the rotationally freed plastic crystalline state (Reference 8) or the translationally freed liquid crystalline state (Reference 9). The 118-121° endotherm for Ib and the 169.5-173° endotherm for Id are both significantly greater in intensity than the corresponding melting point endotherms for these compounds. To our knowledge, this is the first reported case of a plastic or liquid crystalline state being observed in a ferrocene or ruthenocene derivative.

An interesting substantiation of the enhanced oxidation resistance in Id and Ie is the observation that the decomposition points of these compounds are unchanged when obtained in air, whereas Ib and Ic begin to decompose above 190° in air.

TABLE I
MELTING AND DECOMPOSITION POINTS
OF UNSYMMETRICALLY CHLORINATED
FERROCENES

Compound	Melting Point (°C)	Decomposition Point (°C)
Iib	88-90	210-220
Iic	103.5-104.5	200-210
Iid	81-82	180-190
Iie	143-144	150

TABLE II
THERMAL TRANSITIONS OF SYMMETRICALLY CHLORINATED
FERROCENES AND DECAChLORORUTHENOCENE

Compound	Heating Rate (°C/min)	Melting Endotherm (°C)	Other Endotherms (°C)	Decomposition Exotherm (°C)
Ia	20	77	-	303
Ib	5	147	118, 131	*
Ib	20	149	121, 133	280
Ic	5	191	-	252, 254
Ic	20	195	-	279, 299
Id	5	212	154, 169.5	225
Id	20	214	157, 173	247
Ie	5	-	-	245
Ie	20	-	-	270
IIIa	20	-	227, 309	378

*Unobtainable due to sublimation of sample

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE OXIDATION-RESISTANT METALLOCENES - THE THERMAL AND OXIDATIVE STABILITY OF POLYCHLORINATED METALLOCENES			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) May 1969 to October 1970.			
5. AUTHOR(S) (First name, middle initial, last name) Frederick L. Hedberg Harold Rosenberg			
6. REPORT DATE March 1972		7a. TOTAL NO. OF PAGES 14	7b. NO. OF REFS 9
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-71-267	
b. PROJECT NO. 7342			
c. Task No. 734201		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Wright-Patterson Air Force Base, Ohio 45433	
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DD FORM 1 NOV 65 1473

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Perchlorinated Ferrocenes Decachlororuthenocene Oxidation-Resistant Metallocenes Thermally Stable Metallocenes Liquid Crystals						

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