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THE THERMAL AND OXIDATIVE STABILITY OF POLYCHLORINATED METALLOCENES

F. L. HEDBERG and H. ROSENBERG

Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, U.S.A.

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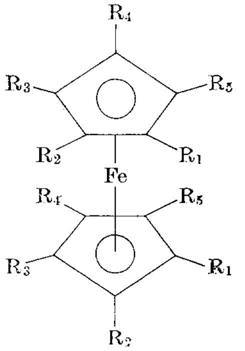
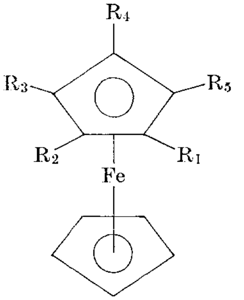
An examination of the thermal and oxidative stability of polychlorinated ferrocenes indicated a decreasing trend in thermal stability and an increasing trend in oxidative stability with increasing chlorine content. The enhanced oxidative stability is best explained on the basis of inductive electron withdrawal from the iron atom by the chlorine atoms. The reduction in thermal stability may also be explained on the basis of the electron-withdrawing inductive effect of the chlorine substituents producing a weakening of the metal-to-ring bonding, although steric crowding due to an eclipsed conformation of the chlorine atoms is also a possible factor in the reduction. 1,1', 2,2'-tetrachloroferrocene and 1,1', 2,2', 3,3', 4,4'-octachloroferrocene were found to exhibit mesophase formation.

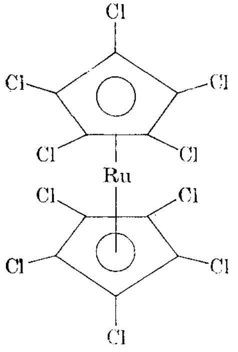
The recently reported [1] synthesis of decachloroferrocene (Ie), decachlororuthenocene (III) and the related polychlorinated compounds (Ib – Id and IIb – IIe) affords an opportunity for investigating the effect of increasing numbers of electron-withdrawing substituents on the thermal and oxidative properties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



Ia. R_1=Cl
Ib. R_1, R_2 = Cl
Ic. R_1, R_2, R_3 = Cl
Id. R_1, R_2, R_3, R_4 = Cl
Ie. R_1, R_2, R_3, R_4, R_5 = Cl



IIa. R_1=Cl
IIb. R_1, R_2 = Cl
IIc. R_1, R_2, R_3 = Cl
IId. R_1, R_2, R_3, R_4 = Cl
IIe. R_1, R_2, R_3, R_4, R_5 = Cl



III

(R_n = H unless otherwise indicated)

Two decasubstituted derivatives of ferrocene have previously been reported, decaethylferrocene [2] and decamethylferrocene [3, 4]. Only the latter compound was fully characterized, with melting points of 277–278° [3] and 291–295° [4] reported. Thus, there appears to be no pronounced destabilizing steric effect from having ten methyl groups on the ferrocene nucleus. Since methyl groups and chlorine atoms 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 substituents on the ferrocene ring breaks down, however, when inductive effects are considered. The electron withdrawal caused by ten chlorine atoms attached to the nucleus might be expected to have a severe weakening effect on either the Fe-ring bonding in Ie or the Ru-ring bonding in III. The much greater ease of oxidation shown by decamethylferrocene versus ferrocene itself may be attributed similarly to the electron-donating characteristic of the methyl group, since electron donors are known to decrease the oxidation potential of ferrocene [5–7].

Electron-withdrawing substituents, on the other hand, have been shown to increase the oxidation potential of ferrocene in an additive manner, both for heteroannular [6] and homoannular [7] substitution. Chloroferrocene was found [5] to oxidize at a potential 0.163 volts higher than ferrocene, while 1,1'-dichloroferrocene was found [6] to oxidize at 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 two to ten chlorine atoms is obviously tenuous. It is interesting, however, to compare the calculated potential difference for decamethlyferrocene versus ferrocene of -0.47 volts (10 times the oxidation potential differential between methylferrocene and ferrocene [5]) with the reported value of -0.43 volts [3].

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° [Ic]. Ferrocene, 1,1'-dichloroferrocene and 1,1', 2,2'-tetrachloroferrocene were oxidized immediately upon contact, giving first the blue color of the corresponding ferricenium 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 ferricenium 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 [1].

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 metallocenes. 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. Although ruthenocene is oxidized immediately by concentrated nitric acid, the perchlorinated derivative was recovered unchanged after 68 hours, demonstrating an enhancement in oxidation stability for the ruthenocene system 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 1. The decomposition points show a downward trend with increasing chlorine content, in accord with the expected destabilizing effect of these electron-withdrawing substituents.

Table 1

Compound	m.p., °C	dec. point, °C
IIb	88–90	210–220
IIc	103.5–104.5	200–210
IId	81–82	180–190
IIe	143–144	150

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 [8]. The results are shown in Table 2. A downward trend in decomposition temperatures with increasing chlorine content is noticeable for Ia – Id. The decomposition of Ie occurs in the solid state and therefore cannot be correlated with the liquid state decomposition occurring with Ia – Id. The significantly higher decomposition temperature 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.

While the downward trend in thermal stability of the polychlorinated ferrocenes with increasing chlorine content may be explained as the result of bond-weakening by inductive withdrawal of electron density by the chlorine substituent, another possibility has emerged as the result of a recent X-ray crystal-

Table 2

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
III	20	—	227, 309	378

* Unobtainable due to sublimation of sample

lographic examination of III and 1,1'-diethoxyoctachloroferrocene [9]. Both of these compounds were found, surprisingly, to exist in the eclipsed conformation. If the other polychlorinated ferrocenes also exist in this conformation, while decamethylferrocene exists in the less-crowded staggered conformation, the decrease in stability of the polychlorinated ferrocenes may be ascribable to steric reasons. The higher stability of III compared to either the polychlorinated ferrocenes or decamethlyferrocene could then be explained by the greater inter-ring chlorine-chlorine distance in IIIa due to the larger ruthenium atom.

Further evidence for a steric, rather than an inductive, explanation for decreasing stability in the polychlorinated ferrocenes is found in the metal-ring distances determined in the X-ray study. While electron withdrawal by the chlorine atom would be expected to give a longer, and therefore weaker, bond in III compared to ruthenocene, a slight shortening was actually observed in the metal-ring distance for III versus that of ruthenocene.

Some interesting anomalies can be seen from the data in Table 2. Ic shows a second decomposition exotherm, indicating some sort of discrete, two-step decomposition for this compound. Compounds Ib, Id and III each have two endotherms below the melting endotherm which, upon visual observation under a hot stage microscope, appear to be transitions to a mesophase. The nature of this mesophase appears to be that of either the rotationally-freed plastic crystalline state [9] or the translationally-freed liquid crystalline state [10]. 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.

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8. The authors wish to thank Dr. G. F. L. Ehlers of the Polymer Branch, Air Force Materials Laboratory for carrying out the differential scanning calorimetric measurements.
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Résumé — L'examen de la stabilité thermique et de la résistance à l'oxydation des ferrocènes polychlorés montre que lorsque la teneur en chlore augmente, la stabilité thermique a tendance à diminuer et la résistance à l'oxydation à augmenter. Ces effets sont expliqués par l'effet inductif électronique respectif des atomes de fer et de chlore. La diminution de la stabilité thermique peut s'expliquer par un affaiblissement de la liaison métal-noyau dû aux substituants chlorés bien que l'encombrement stérique résultant de la configuration éclipsée des atomes de chlore soit aussi un facteur possible. On a trouvé que le tétrachloroferrocène-1,1', 2,2' et l'octachloroferrocène-1,1', 2,2', 3,3', 4,4' pouvaient former une mésophase.

Zusammenfassung — Eine Prüfung der thermischen und Oxidationstabilität von polychlorierten Ferrocenen ergab bei zunehmendem Chlorgehalt eine abnehmende Tendenz der thermischen und eine steigende der Oxidationstabilität. Die erhöhte Oxidationstabilität läßt sich am besten aufgrund der induktiven Elektronen-Entziehung von dem Eisen-Atom durch die Chlor-Atome erklären. Die Abnahme der thermischen Stabilität kann ebenfalls aufgrund des induktiven Elektronen-Entziehungseffektes der Chlorsubstituenten erklärt werden, welcher eine Schwächung der Bindung zwischen Metall und Ring herbeiführt, obwohl auch eine sterische Anhäufung infolge einer abnehmenden Konformation der Chlor-Atome ein möglicher Faktor bei der Abnahme ist. 1,1', 2,2'-Tetrachlorferrocen und 1,1', 2,2' 3,3', 4,4'-Oktachlorferrocen zeigten eine Mesophasenbildung.

Резюме — Изучены термо- и относительная стабильность полихлорированных ферроценов и установлена уменьшающая тенденция термостабильности и увеличивающая тенденция окислительной стабильности при увеличении количества хлора. Увеличенная окислительная стабильность объясняется наилучшей индуктивной отдачей электрона атомом железа к атому хлора. Восстановление также объясняется индуктивным эффектом отдачи электрона к замещающим хлорам, вызывающим ослабление связи металла к кольцу. При восстановлении стерическое затруднение благодаря конформации атомов хлора может быть влияющим фактором.

В случае 1,1', 2,2' — четыреххлористого ферроцена и 1,1', 2,2', 3,3', 4',- — восьмихлористого ферроцена показано образование мезофаза.