# B. Ya. Andreev, L. M. Dyagileva, G. I. Feklissov

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## Abstract

## Full Text

**B. Ya. Andreev, L. M. Dyagileva, G. I. Feklissov**

# Thermal Stability of Ferrocene

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Recently, sandwich compounds have been attracting the attention of an ever wider circle of researchers. They are beginning to interest industry; ferrocene has been proposed ([1]) for use as an antiknock agent, as an additive to mineral oils, and as a thermally stable heat-transfer medium. It is also assumed that, upon decomposition under certain conditions, sandwich compounds may serve as starting substances for the production of metallic powders and films with specified properties, since in them the metal is bound by a special type of bond only to carbon. For this reason, the study of the thermal decomposition of compounds of this type is of undoubted theoretical and practical interest. Up to the present time there have been no data in the literature from a systematic study of this process. Even for ferrocene only information on the temperatures at which its decomposition begins is known, and these data are contradictory. Some authors ([2]) consider ferrocene stable up to 400°C, others ([3]) up to 454°, and still others ([1]) up to 470°. The authors of these works indicate neither the methods of investigation nor the reaction products.

We have carried out a more detailed study of the behavior of ferrocene upon heating. The present communication sets forth the results of studying the isothermal decomposition of ferrocene under static conditions at various temperatures. Under the conditions of our experiments, the initial vapor pressure of ferrocene ($\sim$ 2 atm) was considerably lower than its vapor pressure (10 atm) calculated from the equation given in ([4]). Therefore, by the time decomposition begins, ferrocene is completely sublimed. The thermal decomposition of ferrocene vapor proceeds at practically the same rate in ampoules made of molybdenum and of refractory glass. The results given below were obtained mainly in experiments carried out in ampoules of refractory glass. The kinetic curves obtained are presented in Fig. 1; from them it is evident that the thermal decomposition of ferrocene proceeds in a rather peculiar manner. At all the temperatures investigated, the amount of ferrocene decreases over 10–15 min by approximately 20%. It then remains practically unchanged for a certain time, which we shall hereafter call the "delay time." After this time has elapsed, the amount of ferrocene decreases rapidly. The delay time is the shorter, the higher the temperature. At 470° it is equal to 30 min, while at 400° it exceeds 10 h. The dependence of the delay time on temperature is satisfactorily described by the Arrhenius equation (Fig. 2), with an apparent activation energy of 38 kcal/mole. At present there are still insufficient experimental data for a detailed discussion of the obtained value of the activation energy. After the delay, the thermal decomposition of fer-

rocene proceeds very rapidly, and we were unable to determine the temperature dependence of its rate.

The ampoules in which the decomposition was carried out became covered, 10–15 min after the start of the reaction, with a black deposit. This deposit consists mainly of carbon and iron. We were unable to determine the exact composition of the coating. As the degree of decomposition of ferrocene increases, the thickness of the layers covering the ampoules increases, and at the end of the reaction the ampoules are covered with dense, even layers having a characteristic metallic luster. At the end of the reaction, a certain amount of black powder accumulates at the bottom of the ampoule. Chemical analysis of the solid substances formed during the pyrolysis of ferrocene shows that these compounds decompose with liberation of iron

and carbon. In a number of experiments we followed the accumulation of iron in the course of ferrocene decomposition. The general form of the kinetic curve, plotted in coordinates of the amount of iron liberated in the course of the reaction—time, corresponds to the curve in coordinates of the decrease in the amount of ferrocene—time. However, it should be noted that the amount of iron liberated in the course of the reaction, especially during the induction period, proves to be smaller than the amount contained in the ferrocene that has decomposed. It is possible that in the course of the thermal decomposition of ferrocene other iron compounds are formed, which we have not identified. Only as a result of complete thermal decomposition is all the iron contained in ferrocene liberated in the form of the free metal; it is often pyrophoric. In this process, for each atom of iron there are liberated

[Figure 1 and Figure 2]

**Fig. 1.** Thermal decomposition of ferrocene. Curves **1, 2, 3, 4, 5** were obtained at temperatures of 400, 420, 430, 450, and 470° respectively

**Fig. 2.** Dependence of $\lg \tau$ on reciprocal temperature

about eight atoms of carbon. The qualitative reactions carried out by us using the procedure of [5] show that iron carbide is absent from the products of complete decomposition of ferrocene.

Pyrolysis of ferrocene proceeds from the very beginning with the formation of gaseous products. Chromatographic analysis of the gas phase shows that the principal products of complete decomposition are methane ($\sim$ 75 vol. %) and hydrogen ($\sim$ 25 vol. %), with traces of ethane. The composition of the gaseous products of incomplete decomposition is more complex: in addition to methane and ethane, compounds with a larger number of carbon atoms are present. The curves of pressure increase during the pyrolysis of ferrocene are antibatic to the curves of decrease in the amount of ferrocene. At an initial vapor pressure of ferrocene equal to 140–150 mm Hg, the pressure in the system increases over 10–15 min by 20–30 mm Hg, and then for some time, depending on the temperature, remains unchanged. After the arrest, the pressure rises relatively

rapidly (10–30 min) to the final value (700 mm Hg). These curves were obtained by us according to the procedure described in [6]. In this case the pressure created in the reaction vessel is equilibrated (by a zero manometer filled with a melt of a tin–bismuth mixture) with air, the pressure of which is measured with a mercury manometer. It should be borne in mind that contact of the reaction mixture with heated metals may cause side reactions to occur. However, measurement of the pressure of gases formed after decomposition of ferrocene in sealed ampoules shows that in this case the regularities of pressure change are analogous to those given above. Per mole of ferrocene, on complete thermal decomposition, usually somewhat more than three moles of gaseous products are liberated. Consequently, on the basis of analysis of the solid substances and gases liberated during the complete thermal decomposition of ferrocene, it may be assumed that under the conditions of our experiments it decomposes mainly according to the following scheme:

$$(C_5H_5)_2Fe \rightarrow Fe + 8C + 2CH_4 + H_2. \quad (1)$$

It should be noted that in experiments on the pyrolysis of ferrocene by the method described in work [6], somewhat more than four moles of gases are evolved per mole of decomposed ferrocene. In this case cracking of the organic products proceeds more deeply, and the proportion of hydrogen in the gas phase increases. This may be a consequence of a decrease in the initial vapor pressure of ferrocene (from 2 atm to 150 mm Hg) or of the effect of contact with heated metals.

The peculiar course of the thermal decomposition of ferrocene can be explained by the presence of a number of consecutive and parallel reactions or combinations of a number of heterogeneous and homogeneous stages of the process. To estimate the influence of the walls on this process, a comparison was made of the rates of decomposition of ferrocene in ampoules with different ratios of wall surface area to volume. Packing the ampoules with sections of capillary tubes made of the same glass leads to a slowing of the process, which indicates the presence of heterogeneous stages in the pyrolysis of ferrocene. This is also confirmed by data on the effect of solid products of ferrocene decomposition on the rate of the process. The results of these experiments are presented in Fig. 3. From this figure it is evident that additions of iron to ferrocene have practically no effect on the thermal decomposition of ferrocene. Additions of carbon do not change the general character of the process, but cause a considerable increase in the induction period. This, evidently, can be explained as follows. During the induction period of the reaction, active intermediate products are formed, which subsequently lead to a strong acceleration of the process. Interaction of these products with carbon removes them from the reaction, and because of this the induction period increases. The rate of thermal decomposition of ferrocene is greatly increased by additions of solid substances formed as a result of its complete decomposition (curve 3, Fig. 3). The induction period in this case is practically not observed. This acceleration is the stronger, the larger

Fig. 3. Effect of additives on the thermal decomposition of ferrocene at 430°. Curves 1, 3, and 4 were obtained for additives: 0.1 g of carbon, 0.1 g of iron, and 0.1 g of products of complete decomposition of ferrocene, respectively. Curve 2 was obtained in the decomposition of pure ferrocene.

Figure 1: Fig. 3. Effect of additives on the thermal decomposition of ferrocene at 430°. Curves 1, 3, and 4 were obtained for additives: 0.1 g of carbon, 0.1 g of iron, and 0.1 g of products of complete decomposition of ferrocene, respectively. Curve 2 was obtained in the decomposition of pure ferrocene.

the surface occupied by the products. Decomposition of ferrocene at 430° is completed in 10–15 min if the ampoule in which the reaction is carried out is packed with sections of capillary tubes coated with reaction products from previous experiments. It is interesting to note that prolonged keeping of the solid products of complete decomposition of ferrocene in vacuum under continuous pumping of desorbing gases leads to an increase in their catalytic activity in the decomposition process.

**Fig. 3.** Effect of additives on the thermal decomposition of ferrocene at 430°. Curves **1**, **3**, and **4** were obtained for additives: 0.1 g of carbon, 0.1 g of iron, and 0.1 g of products of complete decomposition of ferrocene, respectively. Curve **2** was obtained in the decomposition of pure ferrocene.

The results obtained, in our opinion, can be explained as follows. During the thermal decomposition of ferrocene, active intermediate substances are formed not only in the bulk, but also on the walls of the reaction vessel in the solid decomposition products. It is possible that such substances are surface compounds of iron with hydrogen and carbon. The formation of these intermediate active substances leads to a strong acceleration of the decomposition process. The possibility of obtaining, in the solid phase, active catalysts for ferrocene decomposition is also indicated by the data of work ([7]) on the synthesis of ferrocene from iron and cyclopentadiene. When vapors of cyclopentadiene are passed in a stream of nitrogen over an iron catalyst for ammonia synthesis at 300°, formation of ferrocene occurs only for 10–15 min and then practically ceases completely. The activity of the iron for the synthesis is restored after alternate oxidation and reduction of it. The iron restored in this way is again active in the synthesis for only 10–15 min. This, in our view, can be explained by the creation, in the course of the synthesis, of catalysts for the decomposition of ferrocene.

Taken together, all the data obtained give grounds for the assumption that the decomposition of ferrocene proceeds by a radical mechanism, and that the regularities of this process are determined by the behavior of atomic hydrogen and the ferrocenyl radical. Chain initiation evidently occurs via the reaction

$$(C_5H_5)_2Fe \rightarrow (C_5H_5)Fe(C_5H_4)^{\cdot} + H^{\cdot}. \qquad (2)$$

This reaction is considerably more probable than direct detachment of the cyclopentadienyl radicals, since the bond energy of these radicals with the metal is very high (286 kcal/mole), while the hydrogen in ferrocene is highly mobile. This is also confirmed by the data of work (3), where formation of diferrocenyl was observed during the thermal decomposition of ferrocene in the condensed phase. It is quite possible that the behavior of hydrogen, diferrocenyl, and the ferrocenyl radical plays the determining role in the regularities of ferrocene decomposition.

Research Institute of Chemistry
at Gorky State University
named after N. I. Lobachevsky

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## CITED LITERATURE

1. A. N. Nesmeyanov, E. G. Perevalova, *Usp. khim.*, **27**, 3 (1958).
2. J. Wilkinson, F. Cotton, *Usp. khim.*, **31**, 838 (1962).
3. G. V. Johns, E. A. McElhill, J. O. Smith, *J. Chem. and Engn. Data*, **70**, 277 (1962).
4. L. Kaplan, W. L. Kester, I. J. Katz, *J. Am. Chem. Soc.*, **74**, 5531 (1952).
5. N. M. Popova, P. V. Zaslavskaya, *Zav. lab.*, **24**, 26 (1958).
6. O. D. Krichevskaya, N. A. Belozerskii et al., *ZhNKh*, **8**, 1806 (1963).
7. S. A. Miller, I. A. Teloth, I. Q. Tremaine, *J. Chem. Soc.*, **1952**, 632.

*Note: Figure translations are in progress. See original paper for figures.*