OXIDATION OF FERROCENE-1,1'-DISULFONIC ACID IN ACID MEDIUM

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The oxidation of ferocene-1,1'-disulfonic acid by ceric sulphate has been studied in aqueous solutions of sulphuric acid at the acidity of medium $H_0 = 0$ to -2. It has been proved that its complete disappearance from the solution is connected with the decomposition of the sandwich structure and necessitates three equivalents of the oxidizing agent. From the time course of the reaction the mechanism of oxidation and decomposition of ferrocene-1,1'-disulfonic acid has been suggested and kinetic parameters of some partial reactions derived.

It is known that ferrocene and most of its derivatives undergo a relatively easy oxidation giving the less stable ferricinium resp. substituted ferricinium cation. Only few papers[1,2] point out a rather complex course of oxidation of ferrocene derivatives carrying electron-attracting substituents. The oxidation needs more than an equivalent amount of oxidizing agent and is accompanied by a relatively rapid decomposition of the sandwich structure of the molecule.

This paper summarizes the results of a study of oxidation of a ferrocene derivative of this type, *viz.* ferrocene-1,1'-disulfonic acid (abbreviation FeX_2). This compound was chosen as a model, because it is readily accesible in pure state and, mainly, because the substance itself as well as its oxidation and decomposition products are well soluble in water and in acid aqueous solutions, too. After a series of experiments ceric sulphate proved to be the most satisfactory oxidizing agent.

EXPERIMENTAL

Reagents. Ferrocene-1,1'-disulfonic acid was prepared and purified according to Nesmejanov and coworkers[3] by reaction of ferrocene with sulphuric acid in acetic anhydride. Its S-benzyl-thiuronium salt melted at 234·5°C, ref.[3] 233—235°C. Cerium(IV) sulphate p.a. (Laboratorchemie, Apolda). Sulphuric acid p.a. 96% (Feinchemie K.‑H. Kallies K.G.). Its aqueous solutions of definite acidity H_0 were prepared according to Hammett and Deyrup[4]. All the other chemicals used were of the p.a. purity grade.

Chromatography. Ascending chromatography on Whatman No 1 paper impregnated with saturated aqueous sodium fluoride solution was used for identification of FeX_2, the mixture acetone–water (7 : 3) being used as eluent. The corresponding R_F value of FeX_2 is 0·55. Fe^{3+} ions remain at the base line in the form of a fluoro complex, whereas they interfere with the FeX_2 spot when non-impregnated paper is used. The spots were made visible by spraying with 0·05M

ceric sulphate in acid medium; blue-green colouration is stable for about two minutes. The spots of Fe^{3+} can be made visible by spraying with concentrated sodium hydroxide solution: brown $Fe(OH)_3$ is formed.

Analytical determination. The presence of ferric ions in solutions after oxidation of FeX_2 was verified qualitatively by reaction with thiocyanate ions, their concentration was determined spectrometrically in the form of the complex with sulphosalicylic acid in solution of pH 2 at a wavelength of 520 nm[5].

Photometric measurements were carried out using the apparatus represented in Fig. 1. *Potential–time curves* were measured by means of the apparatus described by Tockstein[6].

RESULTS

Colour Changes during Oxidation with Ceric Sulphate

The oxidation of yellow FeX_2 solutions with ceric ions is accompanied by a rapid colour change to blue-green. This colouration gradually disappears, and the solution turns yellow again. The time necessary for the disappearance of the blue-green colour depends on the temperature of the solution, its concentration, acidity of medium, and amount of the oxidizing agent added. The original yellow colouration of FeX_2 solutions is due to their absorption in the region of 430 nm, the blue-green colouration is caused by an one-electron oxidation product of FeX_2, *viz.* the disulphonated ferricinium cation (abbreviation FeX_2^+) having an absorption maximum at 655 nm. (Low stability of this one-electron oxidation product prevents a precise measurement
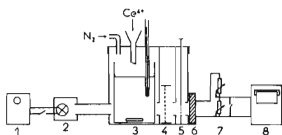

FIG. 1

Scheme of Apparatus for Spectrophotometric Measurements

1 Stabilized source 6 V, *2* lamp (6 V, 0·5 A) *3* 20 ml cell with magnetic stirrer, thermometer and temperation coil, *4* interference filter 651 nm, *5* sliding diaphragm, *6* selenium element, *7* voltage divider, *8* recording microvoltmeter EZ-3.
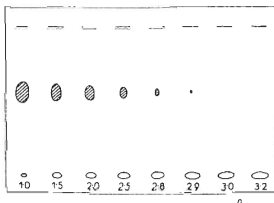

FIG. 2

Chromatographic Picture of the Reaction Mixture FeX_2-Ce^{4+} after Disappearance of FeX_2^+ from the Solution

$2 . 10^{-2}$M-FeX_2, $H_0 = 0$ ($n =$ molar ratio of concentrations Ce^{4+}/FeX_2).

of its absorption curve. From the further text it follows that the decomposition of FeX_2^+ cation is substantially smaller in solutions of high acidity and in the presence of excess cerium(IV) ions, so that it is possible to measure the absorption curve at least in the region where the oxidizing agent does not absorb.) The presence of FeX_2^+ was verified qualitatively by reduction with sulphite solution and subsequent chromatographic identification of FeX_2. The yellow solution resulting after the disappearance of the blue colouration contains either FeX_2 (which was identified chromatographically) or excess oxidizing agent and ferric ions depending on the amount of the oxidizing agent used.

Stoichiometry of the Reaction of FeX_2 with Ceric Sulphate

Fig. 2 presents a chromatographic picture of the reaction mixtures containing the same amounts of FeX_2 and variable amounts of ceric sulphate, each after the disappearance of blue-green colouration *i.e.* complete disappearance of FeX_2^+ from the solution. The molar ratio of the oxidizing agent and FeX_2 at the beginning of the reaction is expressed by the symbol n. From Fig. 2 it can be seen that the spot of FeX_2 gradually weakens and vanishes completely at the ratio $n \geqq 3$. At the same time, the spots of ferric ions at the base line increase which points to an increasing amount of the decomposed sandwich molecules. The dependence of ferric ion content on the amount of oxidizing agent in solutions after disappearance of blue-green colouration can be seen in Fig. 3. The content of ferric ions increases almost linearly with increasing value of the parameter n up to $n = 3$ when the maximum is reached corresponding to equimolecular amount of the original FeX_2 content. The both results confirm the findings of Chen, Refojo and Cassidy[1], *viz.* the necessity of three equivalents of oxidizing agent for complete oxidation of FeX_2. There still remains a question as to the composition and character of products of this three-electron oxidation accompanied by complete decomposition of the sandwich molecule. Ferric ion is one of them; its formation from the formally bivalent iron in FeX_2 needs only one electron. The compounds formed by oxidation of substituted cyclopentadiene rings can be only further products. It is not known which further chemical changes they undergo since the moment of leaving the sandwich molecule. From the solutions we could not isolate any well-defined organic compound, the structure and properties of which would suggest these chemical changes. We shall content ourselves with mere statement that each released substituted cyclopentadiene ring acts as an one-electron reducing agent[7]. (According to our ideas this could be the cyclopentadiene-sulfonic acid formed by decomposition of FeX_2^+, which is known to be a relatively strong one-electron reducing agent[8].) The stoichiometry of the whole three-electron oxidation of FeX_2 is described by Eq. (*A*), where X^- and X_0 represent formally the residue $(C_5H_4SO_3H)^-$ and its one-electron oxidation product, respectively.

$$\{Fe^{2+}(X^-)_2\} + 3\,Ce^{4+} \;\rightarrow\; Fe^{3+} + 2\,X_0 + 3\,Ce^{3+}. \qquad (A)$$
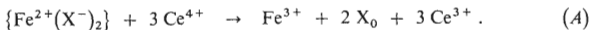
Time Course of the Reaction

The reaction course was studied by two independent methods. The Ce^{4+} concentration change was followed indirectly using the method of currentless curves potential–time developed recently[6,9-14], and the FeX_2^+ concentration change was measured spectrophotometrically.

Potential–Time Curves. From the set of potential–time curves (Fig. 4) it is obvious, first of all, that the complete oxidation is achieved at $n = 3$. The curves are not developed up to $n = 1$; this means that the equilibrium potentials are established immediately. This piece of knowledge is very important. Therefrom it follows that the very rapid one–electron oxidation represented by Eq. (B) is the first step. The

$$FeX_2 + Ce^{4+} \rightarrow FeX_2^+ + Ce^{3+} \qquad (B)$$

curves for $1 < n < 3$ show, after the initial rapid increase, a marked delay followed by a relatively steep potential decrease. The course of the curves is characteristic for a slower redox reaction. Further, we shall focus our attention on these slower processes. A very useful piece of information is supplied by the curve of dependence of angular coefficients (S) of decreasing sections of potential–time curves on the parameter n in the range $1 < n < 3$, which is given in Fig. 5. The plot of $S(n)$ vs n is typical for two competing subsequent redox reactions, the rate constant of the second reaction being greater than that of the first one[14]. The reaction of ceric ions in solution occurs in such a way that, after a very rapid consumption of the first equivalent (Eq. (B)), a slow drawing of the second equivalent and a more rapid
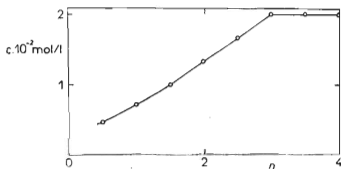

FIG. 3

Dependence of Fe^{3+} Concentration on Parameter n in Solutions of FeX_2 and Ce^{4+} after Disappearance of FeX_2^+
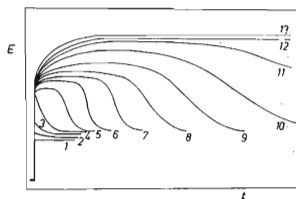 $2 . 10^{-2}$M-FeX_2, $H_0 = 0$.

FIG. 4

A Part of a Set of Potential–Time Curves for FeX_2–Ce^{4+} System ($2.5 . 10^{-3}$M-FeX_2, $H_0 = 0$, temperature 25°C)
    n: 1 0·25, 2 0·5, 3 0·75, 4 1·0, 5 1·2, 6 1·4, 7 1·8, 8 2·0, 9 2·25, 10 2·5, 11 2·75, 12 3·0, 13 3·25.

drawing of the third one follows. According to the relation[14] $\eta = S^*/(2 - n^* - S^*)$ where S^* and n^* are the coordinates of the maximum of the curve $S(n) \sim n$, the ratio of rate constants of the redox reactions of the third and second equivalents of Ce^{4+} was calculated: $\eta = 8.6$. The drawing of the second and third equivalents of Ce^{4+} from the solution is due to a redox reaction with the sulphonated cyclopentadiene rings formed by decomposition of the sandwich molecule.

Spectrophotometric study. Cations FeX_2^+, as the only components of the whole system, absorb in the range of 655 nm. Their slow decomposition makes itself felt by a gradual disappearance of blue-green colouration of solution which makes it possible to follow spectrophotometrically the time course of the reaction. The results of these measurements are given in Fig. 6. Therefrom it is obvious that the dependence $\log(\varepsilon/\varepsilon_0) \sim t$ is linear in the whole range of times measured, so that the decrease of FeX_2^+ follows the kinetic equation of monomolecular reactions. (In informative experiments, the dependences $\log(\varepsilon/\varepsilon_0) \sim t$ were measured for various initial concentrations of FeX_2 solutions. Deviations from linear course were encountered with solutions having the initial concentration lower than 10^{-3}M, and therefore, all the discussion and conclusions concern more concentrated solutions.)

The curves representing the time course of the reaction for $n \leqq 1$ are mutually parallel and their intercepts at the $\log(\varepsilon/\varepsilon_0)$ axis are directly proportional to the parameter n. Thereby the condition of the Lambert–Beer law is fulfilled, and the extinc-
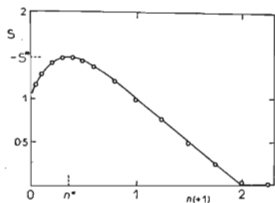
Fig. 5

Dependence of S on Parameter n for FeX_2–Ce^{4+} System

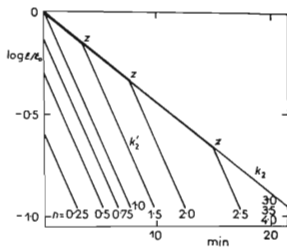$2.5 \cdot 10^{-3}$M-FeX_2, $H_0 = 0$, temperature $25°C$.

Fig. 6

Time Dependence of FeX_2^+ Decrease at Various Values of Parameter n

$4 \cdot 10^{-3}$M-FeX_2, $H_0 = 0$, temperature $25°C$. Ordinates give the ratios of actual extinction to the extinction at the time $t = 0$ of the solutions FeX_2–Ce^{4+} at a wavelength 651 nm.

tions of solutions can be used as a concentration measure of FeX_2^+ and introduced into kinetic equations. The curves for $n \geqq 3$ are identical, the reaction rate is generally lower than that for $n \leqq 1$ and does not further depend on the parameter n. A special shape can be seen in the case of curves for $1 < n < 3$. Up to a certain point (Z), their angular coefficient is identical with that of the curves for $n = 3$, whereas the section of the curve behind the point Z has the angular coefficient identical with that of the curves for $n = 1$. The dependence of the extinction of the point Z on the parameter n is expressed by the relation $\varepsilon_Z = \varepsilon_0 (3 - n)/2$.

The straight lines $n \geqq 1$ go out from one point. This confirms the fact that a quantitative rapid one-electron oxidation of FeX_2 according to Eq. (B) is the first reaction step.

The decomposition of the disulphonated ferricinium cation is accompanied by further redox changes involving, first of all, the sulphonated cyclopentadiene rings which have been designed schematically with the symbol X^-. From the ratio of angular coefficients of functional dependences for curves having $n \leqq 1$ and $n \geqq 3$, which is near to three, we conclude that, in the solution containing maximum one equivalent of oxidizing agent per one equivalent of FeX_2, the free particles X^- reduce the equivalent portion of the cation FeX_2 not yet decomposed. This reaction must be uncomparably more rapid than the decomposition of FeX_2^+. The decrease of these ions is then caused not only by the decomposition but also by the redox reaction (C).
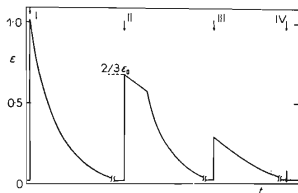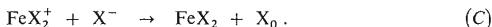
$$FeX_2^+ \; + \; X^- \;\; \rightarrow \;\; FeX_2 \; + \; X_0 \,. \tag{C}$$

FIG. 7

Gradual Titration of FeX_2 with Ceric Sulphate Solution

$3 \cdot 10^{-3}$M-FeX_2, $H_0 = 0$, temperature 25°C, (the extinction of solutions in a 1 cm cell were registered at the wavelength 651 nm). I—IV denote the addition of the 1st to 4th equiv. of Ce^{4+}.
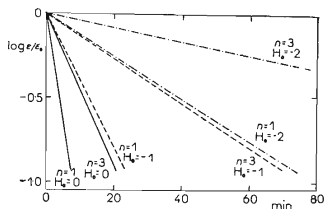

FIG. 8

Dependence of FeX_2^+ Decrease on Acidity of Medium

$4 \cdot 10^{-3}$M-FeX_2, temperature 25°C.

These ideas are justified by the results of gradual titration of FeX_2 solution. If oxidizing agent is added by equivalents to the FeX_2 solution at sufficiently long intervals (after complete disappearance of the blue colouration caused by the preceding addition), it can be found that, after complete reaction with the first equivalent, two thirds of the initial amount of FeX_2 are present in the reaction mixture (Fig. 7). As all the acid FeX_2 is oxidized immediately after the addition of the first Ce^{4+} equivalent, its presence in the solution can only be explained by reduction of FeX_2^+ caused by its own decomposition products according to Eq. (C).

The concentration decrease of FeX_2^+ ions is three times slower in the solutions containing three and more equivalents of the oxidizing agent and corresponds to a simple decomposition of this ion. The reducing particle X^- is drawn by the reaction with Ce^{4+} ions and cannot take part in the reduction of FeX_2^+ cation. The dependences $\log(\varepsilon/\varepsilon_0) \sim t$ for $1 < n < 3$ indicate that the FeX_2^+ ion concentration decreases due only to the decomposition reaction as long as Ce^{4+} ions are present in the solution. Since the moment of complete exhaustion of Ce^{4+} ions, which is characterized by the point Z (Fig. 6), decomposition and reduction of FeX_2^+ ions proceed simultaneously.

Influence of Acidity of Medium

The dependence $\log(\varepsilon/\varepsilon_0) \sim t$ for various ratios (n) of FeX_2 and ceric sulphate was followed in media of various acidity in the range $H_0 = 0$ to -2. The course of the dependences is given in Fig. 8. From the graphs it is obvious that a linear dependence is maintained in all the cases, so that the conclusions concerning the character of the reaction can be considered to be independent of the acidity of medium. If we ascribe the rate constants k_2 and k_2' to the decomposition reaction of FeX_2^+ cation and to the reaction involving the decomposition combined with the reduction of this cation, respectively, we can determine their values from Table I. It turns out that the ratio $k_2' : k_2$ remains about three irrespective of the acidity of medium. Further, it is obvious that the rate of the process decreases roughly $\sqrt{10}$ times when increasing

TABLE I

Rate Constants of Decomposition of FeX_2^+

| Constant	$H_0 = 0$	$H_0 = -1$	$H = -2$
k_2 (s^{-1}); $n \geqq 3$	$1.58 \cdot 10^{-3}$	$4.90 \cdot 10^{-4}$	$1.51 \cdot 10^{-4}$
k_2' (s^{-1}); $n \leqq 1$	$4.80 \cdot 10^{-3}$	$1.47 \cdot 10^{-3}$	$4.50 \cdot 10^{-4}$
k_2'/k_2	2.97	3.00	2.98

the acidity by an H_0 unit. In the medium of $H_0 = -2$, the decomposition rate of FeX_2^+ is sufficiently slow to permit a usual potentiometric titration of FeX_2 with a ceric sulphate solution: from the well-developed titration curves, the approximate value of redox potential of FeX_2^+/FeX_2 can be determined, *viz.* $+0.83$ V under the conditions used.

### *Influence of Temperature on Stability of Disuphonated Ferricinium Cation*

The rate of decrease of FeX_2^+ in the reaction mixture increases with the temperature. It was found that the dependence of the rate constants k_2 and k'_2 on the temperature fulfils the Arrhenius relation in the medium of the acidity $H_0 = 0$ and in the temperature range $15-45°C$. The values 14.4 kcal mol^{-1} and 7.82 and 8.30 have been found for E^+ and log A for k_2 and k'_2 respectively.

DISCUSSION

The first step of the oxidation of FeX_2 is a very rapid quantitative one-electron oxidation of FeX_2 giving an unstable one-electron product -- the disulphonated ferricinium cation (FeX_2^+). This species decomposes slowly to give ferric ion and two particles X^- -- which could be cyclopentadienesulfonic acid with respect to the high acidity of medium. The species X^- acts as an one-electron reducing agent towards the strongest oxidizing agent present in the reaction mixture, *viz.* ceric ions or (in the absence of ceric ions) the cation FeX_2^+. The particle X^- thus vanishes very rapidly according to the Eqs:

$$X^- + Ce^{4+} \rightarrow X_0 + Ce^{3+},$$

or
$$X^- + FeX_2^+ \rightarrow X_0 + FeX_2.$$
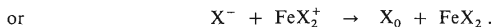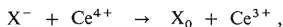
Further, we assume that the decomposition of FeX_2^+ ions proceeds in two steps each producing a particle X^-:

$$FeX_2^+ \xrightarrow{\text{slowly}} FeX^{2+} + X^-$$

$$FeX^{2+} \xrightarrow{\text{more rapidly}} Fe^{3+} + X^-.$$
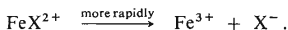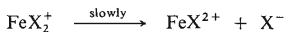
The particle FeX^{2+} could be, according to our ideas, a fragment of the cation FeX_2^+ with one sulphonated cyclopentadiene ring. The whole reaction can be described by the following scheme:
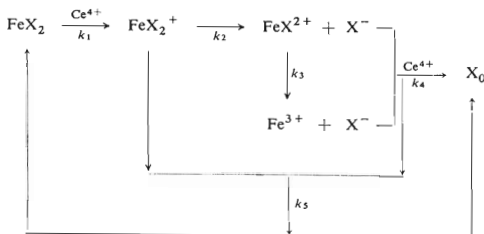
The reaction scheme can be described by following formally kinetic equations (the expressions in brackets denote the actual concentrations of the respective species):

$$-d[FeX_2]/dt = k_1[FeX_2][Ce^{4+}] - k_5[FeX_2^+][X^-], \qquad (1)$$

$$-d[FeX_2^+]/dt = -k_1[FeX_2][Ce^{4+}] + k_2[FeX_2^+] + k_5[FeX_2^+][X^-], \qquad (2)$$

$$d[FeX^{2+}]/dt = k_2[FeX_2^+] - k_3[FeX^{2+}], \qquad (3)$$

$$d[Fe^{3+}]/dt = k_3[FeX^{2+}], \qquad (4)$$

$$d[X^-]/dt = k_2[FeX_2^+] + k_3[FeX^{2+}] - k_4[X^-][Ce^{4+}] - k_5[X^-][FeX_2^+], \qquad (5)$$

$$d[X_0]/dt = k_4[X^-][Ce^{4+}] + k_5[X^-][FeX_2^+], \qquad (6)$$

$$-d[Ce^{4+}]/dt = k_1[FeX_2][Ce^{4+}] + k_4[X^-][Ce^{4+}]. \qquad (7)$$

The above set of equations will be simplified substantially by introducing the following experimentally supported approximations and presumptions:

1. The spectral as well as potentiometric measurements have confirmed that the first reaction step is very rapid. The corresponding constant k_1 is high and, therefore, the first step can be supposed to be finished instantaneously and, hence, the term $k_1[FeX_2][Ce^{4+}]$ need not be considered in Eqs (1), (2) and (7).

2. With respect to the rapid exhaustion of particles X^- from the solution by reaction with Ce^{4+} or FeX_2^+ ions, the concentration of these particles approaches zero and does not change with time, *i.e.* $k_4, k_5 \gg k_2, k_3$; we can, consequently, write the condition of steady state $d[X^-]/dt = 0$ and introduce it into Eq. (5) to obtain Eq. (8).

$$k_2[FeX_2^+] + k_3[FeX^{2+}] = k_4[X^-][Ce^{4+}] + k_5[X^-][FeX_2^+]. \qquad (8)$$

3. The both terms of the right side of Eq. (8) cannot make themselves felt simultaneously. A high potential difference of Ce^{4+}/Ce^{3+} and FeX_2^+/FeX_2 reaching about 0.8 V results in the relation $k_4 \gg k_5$. As long as the concentration $[Ce^{4+}] \neq 0$, the term $k_4[X^-][Ce^{4+}]$ predominates by far; hence, the term $k_5[X^-][FeX_2^+]$ cannot make itself felt before the disappearance of Ce^{4+} from the solution. The participation of Fe^{3+} ions in the overall process is not considered in the reaction scheme for analogous reasons, too. The equilibrium of the system $Fe^{3+} + FeX_2 \rightleftarrows Fe^{2+} + FeX_2^+$ is shifted markedly to the left side of the equation and cannot affect significantly neither the measurements nor the conclusions drawn therefrom.

After these simplifications, the above-mentioned set of kinetic equations is transformed:

a) for $[Ce^{4+}] \neq 0$	*b)* for $[Ce^{4+}] = 0$
i.e. for $n \geqq 3$ or in the	*i.e.* for $n \leqq 1$ or in the
range $1 < n < 3$ until the	range $1 < n < 3$ after the
consumption of Ce^{4+} in	consumption of Ce^{4+} in
the solution:	the solution:

$$[FeX_2] = 0 \tag{1a}$$

$$d[FeX_2]/dt = k_2[FeX_2^+] + k_3[FeX^{2+}] \tag{1b}$$

$$-d[FeX_2^+]/dt = k_2[FeX_2^+] \tag{2a}$$

$$-d[FeX_2^+]/dt = 2k_2[FeX_2^+] + k_3[FeX^{2+}] \tag{2b}$$

$$d[FeX^{2+}]/dt = k_2[FeX_2^+] - k_3[FeX^{2+}] \tag{3}$$

$$d[Fe^{3+}]/dt = k_3[FeX^{2+}] \tag{4}$$

$$d[X^-]/dt = 0 \tag{5}$$

$$d[X_0]/dt = k_2[FeX_2^+] + k_3[FeX^{2+}] \tag{6}$$

$$-d[Ce^{4+}]/dt = k_2[FeX_2^+] + k_3[FeX^{2+}] \tag{7a}$$

$$[Ce^{4+}] = 0 \tag{7b}$$

The relation $(7a)$ is very important, because it shows that the velocity of decrease of Ce^{4+} in the solution is controlled by the decomposition velocity of FeX_2^+ and FeX^{2+}, *i.e.* these two decomposition reactions represent, with respect to Ce^{4+}, two subsequent competing reactions. Therefore, the parameter computed from the dependence $S(n) \sim n$ directly corresponds to the ratio $\eta = k_3/k_2 = 8.6$ or, in other

words, the reaction rate constant of the splitting off of the second substituted ring is 8·6 times higher than that of the splitting off of the first ring. In this connection it will be interesting to mention that the dissociation energy of splitting of the first ring in ferrocene molecule (6·63 eV) is roughly eleven times greater than that of the second ring (0·6 eV) (ref.[15]).

As the ratio k_3/k_2 is relatively high, it can be presumed that FeX^{2+} attains the steady state soon after the beginning of the reaction, *i.e.* $d[FeX^{2+}]/dt = 0$, wherefrom it follows that

$$k_2[FeX_2^+] \approx k_3[FeX^{2+}]$$

and after introducing into Eq. (2b)

$$-d[FeX_2^+]/dt \approx 3k_2[FeX_2^+],$$

i.e. the rate of decrease of FeX_2^+ in the absence of Ce^{4+} $(n \leqq 1)$ is three times greater than that in the presence of Ce^{4+} $(n \geqq 3)$ which agrees with the angular coefficients of straight lines in Fig. 6. The value $3k_2$ is then identical with the constant k_2'.

Thus, the mechanism proposed stands in accord with all the experimental facts and can be considered as a good approximation for description of oxidation of ferrocene-1,1'-disulfonic acid in acid medium.

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