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A. V. SAVITSKII and Corresponding Member of the Academy of Sciences of the USSR Ya. K. SYRKIN

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Abstract

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KINETICS OF THE OXIDATION OF FERROCENE BY IODINE

The reaction of conversion of ferrocene into the ferricinium ion is of interest as a process of electron transfer under solution conditions. The mechanisms of such reactions have been studied repeatedly, especially in the case of similarly charged ions. Thus, for example, in the isotopic reaction between Fe^{2+} and Fe^{3+}, the process possibly proceeds with the participation of water molecules forming a chain along which the electron is transferred ([1–3]). Because of the large electrostatic repulsion of similarly charged ions, the reaction must proceed at a sufficiently large distance. Such reactions may be characterized by small transmission coefficients.

In the case of the electroneutral molecules of ferrocene $Fe(C_5H_5)_2$ (hereafter abbreviated as Fn) and iodine, electron transfer can occur over a small distance.

It is natural to propose two possible schemes for the course of the reaction

$$\left.\begin{aligned} \mathrm{Fn} + \mathrm{J}_2 &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fn}^+ + \mathrm{J}_2^- \\ \mathrm{Fn} + \mathrm{J}_2^- &\xrightarrow{k_3} \mathrm{Fn}^+ + 2\mathrm{J}^- \end{aligned}\right\} \qquad \text{Scheme 1}$$

or

$$\left.\begin{aligned} \mathrm{Fn} + \mathrm{J}_2 leftarrows \mathrm{Fn}^+ + \mathrm{J} + \mathrm{J}^- \\ \mathrm{Fn} + \mathrm{J} arrow \mathrm{Fn}^+ + \mathrm{J}^- \end{aligned}\right\} \qquad \text{Scheme 2}$$

In a number of reactions it has been shown ([4–6]) that decomposition of J_2^- into J and J^- is not observed in solution. In this connection Scheme 1 is more probable. It may be assumed that k_2 and k_3 are quantities of the same order. This is explained by the instability of the radical ion J_2^-, which reacts rapidly both with a ferrocene molecule and with a ferricinium ion. Thus, for example, the reaction

$$2Fe^{3+} + 2J^- = 2Fe^{2+} + J_2$$

proceeds through the stages

$$Fe^{3+} + 2J^- \underset{k_a}{\rightleftharpoons} Fe^{2+} + J_2^-$$

and

$$Fe^{3+} + J_2^- \xrightarrow{k_b} Fe^{2+} + J_2,$$

with $k_a \approx 0.2\, k_b$ ([5]). The reaction of $Fe(CN)_6^{3-}$ with iodide proceeds by an analogous mechanism; in this case $k_a = 4.3\, k_b$ ([6]). If it is assumed that J_2^- does not accumulate during the reaction, the following expression is obtained for the rate of oxidation of ferrocene:

$$\frac{d[Fn^+]}{dt} = \frac{2k_1 k_3 [Fn]^2 [J_2]}{k_2[Fn^+] + k_3[Fn]}, \tag{1}$$

which, in the case $k_2 \approx k_3$, takes the form:

$$\frac{d[Fn^+]}{dt} = \frac{2k_1 [Fn]^2 [J_2]}{[Fn]_0}, \tag{2}$$

where $[Fn]_0$ is the initial concentration of ferrocene.

It is possible that the reaction proceeds with preliminary formation of the molecular compound FnJ_2, in which ferrocene is the electron donor. There are data on the existence of complexes of ferrocene with halogenated hydrocarbons (7), although it is known that the latter have a significantly lower ability to form molecular compounds with electron transfer than iodine. Formation of FnJ_2 may affect the shape of the kinetic curves at high concentrations of ferrocene and iodine, when the equilibrium

$$Fn + J_2 leftarrows FnJ_2$$

is shifted considerably to the right. If the process proceeds through formation of FnJ_2, then the peculiarity of the reaction consists in the fact that 1) FnJ_2 is formed without activation energy, 2) upon formation of the molecular compound the molecule is polarized, and 3) electron transfer from ferrocene to iodine in the molecular compound probably proceeds more readily than in a bimolecular reaction.

The oxidation of ferrocene by iodine was studied by us in 93 and 96% alcohol at initial ferrocene concentrations not exceeding 10^{-4} mole $\cdot$ l^{-1} and with a 15-50-fold excess of iodine in the temperature interval 5–40°. The concentration of ferricinium ions was determined spectrophotometrically from the absorption maximum at 619 mμ on an SF2M instrument under thermostated conditions. On the basis of the data obtained it was established that, in excess iodine, the equilibrium

$$\mathrm{Fn} + {}^{3}/{}_{2}\mathrm{J}_2 leftarrows \mathrm{Fn}^{+} + \mathrm{J}_3^{-}$$

is shifted toward ion formation. With a 25-fold excess of iodine and at a temperature of 25°, the equilibrium concentration of ferricinium ions is approximately equal to 98% of the initial ferrocene concentration. Thus, the rate of the reverse reaction under the experimental conditions is relatively small, and therefore it may be neglected in studying the kinetics of ferrocene oxidation. The side reaction of iodine with the solvent (8) has no substantial effect on the course of the main reaction, since the latter proceeds considerably faster. Under the experimental conditions, the greater part of the ferrocene is oxidized by iodine within several minutes.

The course of the change in the concentration of ferricinium ions in each experiment is described by the equation

$$\frac{d[\mathrm{Fn}^{+}]}{dt} = k'\left([\mathrm{Fn}]_0 - [\mathrm{Fn}^{+}]\right)^2, \qquad (3)$$

where k is a constant quantity. When the initial concentrations of ferrocene and iodine are changed, the character of the kinetic curves is preserved; however, the magnitude k changes proportionally to $[\mathrm{J}_2]_0/[\mathrm{Fn}]_0$, where $[\mathrm{J}_2]_0$ is the initial iodine concentration (see Table 1).

The experimental equation (4) for the rate of oxidation of ferrocene agrees with equation (2), derived for the first reaction scheme:

$$\frac{d[\mathrm{Fn}^{+}]}{dt} = \frac{k'\left([\mathrm{Fn}]_0 - [\mathrm{Fn}^{+}]\right)^2 [\mathrm{J}_2]_0}{[\mathrm{Fn}]_0}. \qquad (4)$$

Thus, the kinetic data do not contradict the assumption of intermediate formation of the unstable radical ion J_2^{-}.

The activation energy and the pre-exponential factor for electron transfer from ferrocene to iodine were determined graphically from the temperature

Table 1

Reaction of ferrocene with iodine in 96.5% alcohol at 25°

Experiment no.	$[Fn]_0$, 10^{-4} mol·l^{-1}	$[J_2]_0$, 10^{-4} mol·l^{-1}	k, $l \cdot mol^{-1} \cdot sec^{-1}$	$k' = k[Fn]_0/[J_2]_0$, $l \cdot mol^{-1} \cdot sec^{-1}$
1	0.463	7.75	256	15.3
2	0.463	15.5	669	20.0
3	0.463	27.1	1100	18.8
4	0.925	15.5	335	20.0
5	0.925	31.0	558	16.7
6	0.925	31.0	707	21.1
7	1.85	7.75	58*	13.9
8	1.85	15.5	178*	21.2
9	1.85	31.0	299	17.8
10	1.85	31.0	300	17.9

* Found from the initial reaction rate.

dependence of the reaction rate. The values of k_1 at different temperatures are given in Table 2.

Experiment gives an activation energy of 14.6 $kcal \cdot mol^{-1}$ and a pre-exponential factor of $9 \cdot 10^{11}$ $l \cdot mol^{-1} sec^{-1}$ ($\Delta S^{\#} = -5.85$ $cal \cdot mol^{-1} \cdot deg^{-1}$). From the corresponding cyclic process one can estimate the solvation energy of the ferricinium ion. It must be greater than 50 $kcal \cdot mol^{-1}$. The comparatively large solvation energy makes it possible to suppose that the positive charge of this ion is located to a considerable extent on the iron atom.

The pre-exponential factor differs little from the usual value. It should be borne in mind that if the reaction proceeds through the molecular compound FnJ_2, then the observed activation energy is equal to the true value decreased by the heat effect of the reaction forming the molecular compound.

Table 2

Values of the rate constant of the reaction
$Fn + J_2 = Fn^+ + J_2^-$

Temperature, °C	Alcohol concentration, %	$k_1 = \frac{1}{2}k'$, $l \cdot mol^{-1} \cdot sec^{-1}$
5.4	93	3.0 ± 0.3
20.0	93	10.6 ± 1.2
21.0	93	11.1
30.0	93	27.3 ± 1.8
40.0	93	52.6
25.0	96.5	9.1 ± 1.0

The observed activation entropy in this case is equal to the sum of the entropy of the reaction forming the molecular compound and the activation entropy of the reaction whose rate is being measured. It should be noted that in electron-transfer reactions between ions of like charge the activation entropy reaches appreciable negative values ([9]). In our case the conditions for electron transfer are apparently quite different, and there are no reasons that would account for a low value of the pre-exponential factor.

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