THE SOLVATION OF THE FERRICENIUM ION

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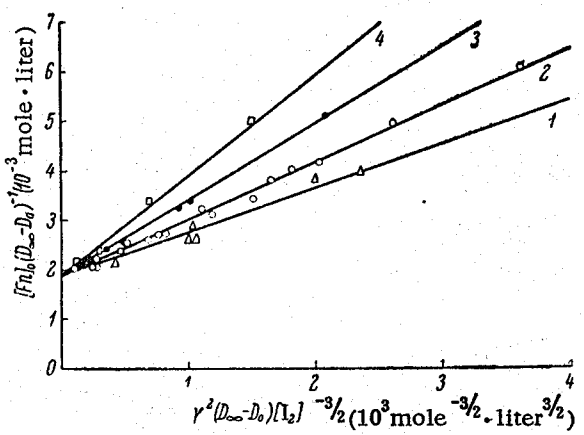
In a previous communication [1] on the basis of ideas of the mechanism of oxidation of ferrocene by iodine, we have suggested that the energy of solvation of the ferricenium ion should be comparatively high. In order to test this suggestion, we report in the present paper a spectrophotometric study of the equilibrium $Fn + \frac{3}{2} I_2 = Fn^+ + I_3^-$ * in alcohol at different temperatures in the range 15-45°. Knowing the heat effect of this reaction, we can calculate the energy of solvation of the ferricenium ion from the corresponding cyclic process.

METHODS AND RESULTS

A sample of iodine and the ferrocene solution were placed in a thermostatically controlled cuvette (d 1.00 cm). The spectrum of the solution was recorded in the region of absorption by the ferricenium ion (580-660 mμ) on a two beam SF2M spectrophotometer. The time of reaching equilibrium in the experiments did not exceed 30 minutes.



Determination of equilibrium constant for the reaction $Fn + \frac{3}{2} I_2 = Fn^+ + I_3^-$ in alcohol (0.25% water), 616 mμ; layer 1 cm. 1) 15°, 2) 25°, 3) 35°, 4) 45°.

The initial ferrocene concentration was so set that the iodide occurred in the form of triiodide and the ion of the latter was not especially associated with the ferricenium ion. The experiments were carried out with some excess of iodine and at ferrocene concentrations from $2.5 \cdot 10^{-4}$ to $\cdot 10^{-3}$ and iodine from 10^{-3} to $1.2 \cdot 10^{-2}$ mole·liter^{-1}. Under equilibrium conditions the ionic strength of the solution did not exceed 10^{-3} mole·liter^{-1}. Therefore in calculating the equilibrium constant it was possible with a sufficient degree of accuracy to take the activity coefficient for ferrocene and iodine as unity, and the activity coefficient of the ions was calculated by the Debye limiting law.

If the reaction $Fn + \frac{3}{2} I_2 = Fn^+ + I_3^-$ is not complicated by side reactions and the Lambert-Beer law is obeyed for all the molecules and ions present, then the relation between the optical density of the solution D_∞ at equilibrium and the initial concentrations $[Fn]_0$ and $[I_2]_0$ is given by the equation

$$[Fn]_0 (D_\infty - D_0)^{-1} = \Delta\varepsilon^{-1} + K^{-1}\Delta\varepsilon^{-2}\gamma^2 (D_\infty - D_0)[I_2]^{-3/2},$$

* Fn means $(C_5H_5)_2Fe$.

where: $D_0=\epsilon_{Fn}[Fn]_0+\epsilon_{I_2}[I_2]_0$; $\Delta\epsilon=\epsilon_{Fn^+}+\epsilon_{I_3^-}-\epsilon_{Fn^-}-\frac{3}{2}\epsilon_{I_2}$, K is the equilibrium constant, γ the activity coefficient for the singly charged ion, ϵ the absorption coefficient for the molecules or ions, $[I_2]$ the iodine concentration at equilibrium, which differs little from $[I_2]_0$ if the iodine is in excess.

This equation shows that between $[Fn]_0(D_\infty-D_0)^{-1}$ and $\gamma^2(D_\infty-D_0)[I_2]^{-\frac{3}{2}}$ there should be a linear relation. In order to determine $\Delta\epsilon$ and K using this equation it is necessary to know the values of γ and $[I_2]$. The latter were found by the method of successive approximations. In this calculation the initial values were $\gamma=1$ and $[I_2]=[I_2]_0$. In later approximations γ and $[I_2]$ were found by the relationship $[Fn^+]=\Delta\epsilon^{-1}(D_\infty-D_0)$. The figure shows the relation after a series of approximations when the given and obtained values of $\Delta\epsilon$ agree.

TABLE 1

Values of K and $\Delta\epsilon$ for Different Temperatures at λ 616 mμ; solvent, ethyl alcohol (0.25% water)

Temperature	$\Delta\epsilon$ ($cm^{-1}\cdot mole^{-1}\cdot liter$)	K, $mole^{-1/2}\cdot liter^{1/2}$	Number of experiments
15.0°	546	3.75	7
25.0	531	3.15	22
35.0	533	2.32	5
45.0	547	1.53	4

TABLE 2

Thermodynamic Data for Reaction $Fn + \frac{3}{2} I_2 = Fn^+ + I_3^-$ in Alcohol at 25°

Percent water in alcohol	$\Delta H°$ (kcal·mole^{-1})	$\Delta S°$ (e. u.)	$\Delta F°$ (kcal·mole^{-1})
0.25	—5.5	—16	—0.675
3.5	—5.5	—14	—1.37

In Table 1 we give the values for $\Delta\epsilon$ and K for different temperatures found by ΔH^0, ΔS^0, ΔF^0 for the reaction (Table 2).

From the values obtained for $\Delta\epsilon$ for different wavelengths we determined the absorption coefficients for the ferricenium ion (Table 3).

DISCUSSION OF RESULTS

For finding the solvation energy of the ferricenium ion we consider the cyclic process:

$$Fn^+_{(g)}+e=Fn_{(g)}+I$$
$$I^-_{(g)}-e=I_{(g)}-E$$
$$Fn_{(g)}=Fn_{(solid)}+\lambda_{Fn}$$
$$I_{(g)}=\tfrac{1}{2}I_{2(g)}+\tfrac{1}{2}D$$
$$\tfrac{1}{2}I_{2(g)}=\tfrac{1}{2}I_{2(solid)}+\tfrac{1}{2}\lambda_{I_2}$$
$$Fn_{(solid)}=Fn_{(alc)}+q_{Fn}$$
$$\tfrac{1}{2}I_{2(solid)}=\tfrac{1}{2}I_{2(alc)}+\tfrac{1}{2}q_{I_2}$$
$$Fn_{(alc)}+\tfrac{3}{2}I_{2(alc)}=Fn^+_{(alc)}+I_3^-{}_{(alc)}+Q$$

$$I_3^-(alc) = I_2(alc) + I^-(alc) + Q_0$$
$$Fn^+_{(g)} + I^-_{(g)} = Fn^+_{(alc)} + I^-_{(alc)} + L_{Fn^+} + L_{I^-}$$

TABLE 3

Absorption Spectra in Alcohol (0.25% water) at 25°

λ (mμ)	Δε	ε_{I_3}	ε_{Fn}(cm^{-1} × × mole^{-1}. l)	$\varepsilon_{I_3^-}$	ε_{Fn^+}
580	384	47.8	0.8	80	377
600	465	32.3	0.6	53	461
616	531	23.8	0.5	35	532
620	527	22.0	0.5	32	529
640	241	14.8	0.4	18	246
660	51	9.8	0.4	10	56

TABLE 4

Sum of Solvation Energies of Cation M^+ and Anion I^- in Ethyl Alcohol

M+	Li+	Na+	K+	Rb+	Cs+	Fn+	$(CH_3)_4N^+$	$(C_2H_5)_4N^+$
$L_{M^+} + L_{I^-}$ (kcal · mole^{-1})	199	170	162	147**	137**	129	100	90
Ionic radius (A)	0.60	0.95	1.33	1.48	1.69	—	3.00	3.63

In the calculations we used the following values (in kcal·mole^{-1}): I =162.5[2], E=74.6[3], λ_{Fn}=19.9[4], D=36.0[5], λ_{I_2}=14.8[5], q_{Fn}=-5.0,* q_{I_2}=-1.65[6], Q_0=-3.6[7] for the reaction in water. The value for Q_0 for alcohol could differ from the value for water, evidently, by not more than 2 kcal·mole^{-1}. The sum of the solvation energies of ions of ferricenium and iodide $L_{Fn^+}+L_{I^-}$ is about 129 kcal·mole^{-1}. This value in Table 4 is compared with the sum of the solvation energies $L_{M^+}+L_{I^-}$ for other cations M^+.

From the relation of solvation energy to ionic radius (Table 4) we can determine the effective solvation radius of the ferricenium ion which is equal to about 2 A. In the electrically neutral ferrocene molecule the distance Fe-C is 2.04 A; in the ion this distance can be somewhat less. The comparatively small value for the solvation radius and the large solvation energy can be understood if we assume that the positive charge of the ion is chiefly concentrated on the atom of iron.

The oxidation of ferrocene by iodine is of interest as an ionic equilibrium in a nonaqueous medium. Approximate calculations [8] based only on calculation of the electrostatic interaction of the ions with the medium show that with decreased dielectric permeability of the medium the entropy of solvation of the ions should assume a more negative value. This conclusion is confirmed by comparison of the data on dissociation of tetrabutylammonium picrate in chlorobenzene [9] (ΔS^0=20 e.u) and the base of Malachite green in water [10] (ΔS^0=+4 e. u.). Thus the negative value of ΔS^0 (Table 2) is not unexpected. The relation of solvation entropy of the ion to dielectric permeability of the medium also agrees with our data on equilibrium in alcohol with different water contents. As the data of Table 2 show, lowering the water concentration leads to a decreased ΔS of the reaction.

* Private communication from O. M. Gaissinskaya and V. A. Sokolov.

** Values for methyl alcohol. The sum of solvation energies for other ions in methyl and ethyl alcohols are very close to each other.

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SUMMARY

1. We have determined the equilibrium constants for the reaction of oxidation of ferrocene by iodine in ethyl alcohol at 15, 25, 35, and 45°. We have calculated values for ΔH^0 and ΔS^0 : ΔH^0=-5.5 kcal·mole^{-1} and ΔS^0=-16 e. u.

2. We have showed that the solvation energy of the ferricenium ion has a relatively large value.

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*Original Russian pagination. See C. B. translation.