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RELATIONSHIP BETWEEN THE IONIZATION POTENTIALS AND THE HALF-WAVE POTENTIALS OF SOME TRIS(2,4-DIKETONATO)RUTHENIUM(III) COMPLEXES

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The first ionization potentials of five tris(2,4-diketonato)-ruthenium(III) complexes determined from their UV photoelectron spectra increase with the increase in the reversible half-wave potentials for the one-electron oxidation of the complexes in acetonitrile. The relationship is explained in terms of the interaction between the non-bonding orbital of acetonitrile molecule and the LUMO of the chelate system of the Ru^{IV} species.

Instances are known of linear relation between the ionization potentials of aromatic compounds in vacuum and the reversible half-wave potentials for their electrochemical one-electron oxidation in various solvents.[1)] For metal complexes, only few data of ionization potentials are available. But similar relation has been reported for a series of ferrocene derivatives in two kinds of solvents.[2)]

Here another example of such relation is presented: there is a nearly linear relationship between the adiabatic ionization potential, $P_{i,a}$, and the reversible half-wave potential, $E^{r}_{1/2}$, of one-electron oxidation in acetonitrile for a series of tris(2,4-diketonato)ruthenium(III) complexes, which covered a much wider potential range than the above-mentioned ferrocene series.

The five complexes listed in Table 1 were prepared according to the "ruthenium blue" method previously reported.[3)] Each of these complexes except **5** showed

Table 1. Reversible half-wave potential ($E^r_{1/2}$) and adiabatic ionization potential ($P_{i,a}$) of [$Ru^{III}(R_1CO\text{-}CH\text{-}COR_2)_3$]

Complex	R_1	R_2	$E^r_{1/2}/V$[a]	$P_{i,a}/V$
1	$-C(CH_3)_3$	$-C(CH_3)_3$	0.46	6.27
2	$-CH_3$	$-CH_3$	0.63	6.50
3	$-CF_3$	$-C(CH_3)_3$	1.32[b]	7.52
4	$-CF_3$	$-CH_3$	1.31[b]	7.33
5	$-CF_3$	$-CF_3$	(1.80)[c]	8.54

a) $E^r_{1/2}$ for [$Ru^{III}L_3$] = [$Ru^{IV}L_3$]$^+$ + e^-, in 0.1 mol dm^{-3} Et_4NClO_4–acetonitrile at 25 °C, obtained from the normal pulse voltammograms at a stationary platinum disk electrode recorded vs. Ag|0.1 mol dm^{-3} $AgClO_4$ (acetonitrile).

b) Quasi-reversible step; $E^r_{1/2}$ is estimated by the extrapolation method.

c) Estimated value (see text).

a one-electron oxidation step in 0.1 mol dm^{-3} Et_4NClO_4–acetonitrile. The step was nernstian for **1** and **2**, and quasi-reversible for **3** and **4**; the $E^r_{1/2}$ values of the latters were determined by the conventional extrapolation method.[4)] The $E^r_{1/2}$ value for **5**, which was not experimentally observable within the potential window (-2.2 V – +1.7 V), was estimated on the basis of the linear relationship established between $E^r_{1/2}$ and the sum of the Hammett constants of the substituents on the ligands.[5)] Almost the same value was obtained also from the extrapolation of the linear dependence of $E^r_{1/2}$ on the ligand-composition of two series of mixed-ligand complexes ([$RuL_n(acac)_{3-n}$] and [$RuL_nL'_{3-n}$] with n = 0 and 1, where L is 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and L' is 2,2,6,6-tetramethyl-3,5-heptanedione).[6)]

The adiabatic ionization potentials of these complexes were obtained from their ultraviolet photoelectron spectra (UPS). The apparatus and the method of the UPS measurement have been described elsewhere.[7)]

The relation between $E^r_{1/2}$ and $P_{i,a}$ can be derived by considering an energy cycle in which gaseous [$Ru^{IV}L_3$]$^+$ is reduced by solid silver in vacuum to produce gaseous [$Ru^{III}L_3$] and gaseous Ag^+ and then these species are brought into 0.1 mol dm^{-3} Et_4NClO_4–acetonitrile solution. The result is

$$E^r_{1/2} - P_{i,a} = \frac{1}{F}\{\Delta G^\circ_{solv}(Ru^{IV}) - \Delta G^\circ_{solv}(Ru^{III})\} + C \qquad (1)$$

where C is the terms arising from the reactions of Ag species and is a constant for a given reference electrode; $\Delta G^\circ_{solv}(Ru^{IV})$ is the standard Gibbs energy of the solvation reaction $[Ru^{IV}L_3]^+(g) = [Ru^{IV}L_3]^+(AN)$ and $\Delta G^\circ_{solv}(Ru^{III})$ is that of the reaction $[Ru^{III}L_3](g) = [Ru^{III}L_3](AN)$.[8] Note that the reference system for each solvated complex is the infinitely dilute solution of the complex in 0.1 mol dm^{-3} Et_4NClO_4–acetonitrile solution with the standard concentration of 1 mol dm^{-3}.

The term $E^r_{1/2} - P_{i,a}$ is obtained from the values in Table 1 and plotted against $P_{i,a}$ (Fig. 1). It becomes negatively large with increasing $P_{i,a}$. As mentioned above, $E^r_{1/2}$ (hence $P_{i,a}$ as seen in Table 1) becomes more positive when the substituents on the ligands are more electron-accepting.[5] It follows that electron-accepting substituents make $\Delta G^\circ_{solv}(Ru^{IV}) - \Delta G^\circ_{solv}(Ru^{III})$ more negative. In other words, the electron-accepting substituents increase the stability of the solvated species and the Ru^{IV} species is more stabilized than the Ru^{III} species.

This observation can be rationalized as follows, if the effect of the substituents on the solvation energies is attributable mainly to a kind of CT interaction between the non-bonding orbital of acetonitrile molecule and the π-system of the chelate ring. Acetonitrile molecules will solvate the complex species with their nitrogen-ends oriented towards the central atom so that the non-bonding orbital of the nitrogen atom can interact with the π-orbital (LUMO) of the chelate ring. The energy level of the LUMO of the Ru^{IV} species lies higher than that of the non-bonding orbital of the nitrogen atom, and the energy level of the LUMO of the Ru^{III} species lies still higher. When electron-accepting substituents are introduced they lower the LUMO, and the energy gap between the LUMO of the π-orbital and the non-bonding orbital is reduced; as a result, the solvation is favored. However, the extent of the lowering of the LUMO will be roughly the same in the Ru^{IV} species as in the Ru^{III} species for given substituents. Therefore, the stabilizing

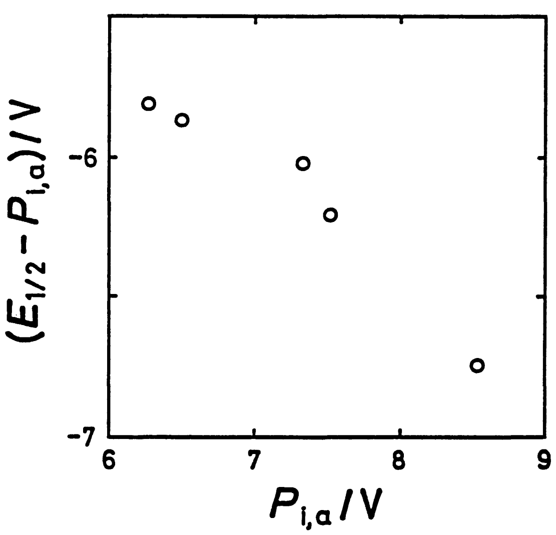

Fig. 1. $E^r_{1/2} - P_{i,a}$ as a function of $P_{i,a}$.

effect of the electron-accepting substituents on the solvation will be more pronounced for $[Ru^{IV}L_3]^+$ than for $[Ru^{III}L_3]$. The stabilization increases with the lowering of the LUMO not linearly but more steeply. This fact seems to be reflected in the upward-convex appearence of the distribution of the points in Fig. 1.

The validity of this explanation will be tested by examining the relationship between $E^r_{1/2}$ in various solvents and $P_{i,a}$ of the same series of complexes.

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7) Because of low vapor pressures of the samples, a heated photoionization chamber was used, and photoelectron counts were accumulated for a long period with an automatic energy calibration system. See M. Takahashi, I. Watanabe, S. Ikeda, M. Kamata, and S. Otsuka, Bull. Chem. Soc. Jpn., 55, 3757 (1982) and M. Takahashi, I. Watanabe, and S. Ikeda, J. Electron Spectrosc. Relat. Phenom., 37,275 (1985).

8) Equation 1 is derived with the following premiss:(a) $FP_{i,a}$ is the standard Gibbs energy of reaction $[Ru^{III}L_3](g) = [Ru^{IV}L_3]^+(g) + e^-(g)$ (the small entropy term is neglected) and (b) the standard potential of reaction $[Ru^{IV}L_3]^+(AN) + Ag(s) = [Ru^{III}L_3](AN) + Ag^+(AN)$ in 0.1 mol dm^{-3} Et_4NClO_4–acetonitrile solution can be approximated by $E^r_{1/2}$.

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