Facile Formation of the Radical Trianion of 4,7-Phenanthroline as Studied by E.S.R. Spectroscopy

Hideo Fujita[a]* **and Hiroaki Ohya-Nishiguchi**[b]

[a] *Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan*
[b] *Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan*

The radical trianion of 4,7-phenanthroline, formed by the chemical and electrochemical reductions in 1,2-dimethoxyethane, has been characterized by e.s.r. spectroscopy, cyclic voltammetry, and McLachlan's MO calculation.

Recently radical trianions of aromatic hydrocarbons[1] and heteroaromatic compounds with substituents[2] have been characterized by e.s.r. and electron nuclear double resonance spectroscopies.[3] The distributions of the unpaired electrons on their molecular orbitals are quite different from those of the corresponding radical anions. From this feature some new routes for synthesis are expected using the trianions as starting materials or intermediates in organic reactions. Therefore, it is important to investigate the organic as well as physical properties of the trianion radicals.[1—4]

During reinvestigation of the electronic structure of 4,7-phenanthroline (**1**) we found, by chance, its trianion radical $(\mathbf{1}^{3-\cdot})$. In this Communication we wish to describe the results of cyclic voltammetry of (**1**) and e.s.r. spectroscopy of $(\mathbf{1}^{3-\cdot})$, and interpret the results based on the McLachlan's MO calculation.[5]

The cyclic voltammogram (CV) of (**1**) was measured in *N*,*N*-dimethylformamide (DMF) in the presence of tetrapropylammonium perchlorate (TPAP) under the conditions described in the literature.[6] During the cathodic sweep of the voltage, three reduction waves clearly appeared. During the anodic sweep, the second wave was very small compared to the others. The half-wave reduction potentials ($E_{1/2}$) were

$$(\mathbf{1}) \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1}^{-\cdot}) \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1}^{2-}) \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} (\mathbf{1}^{3-\cdot})$$

Scheme 1

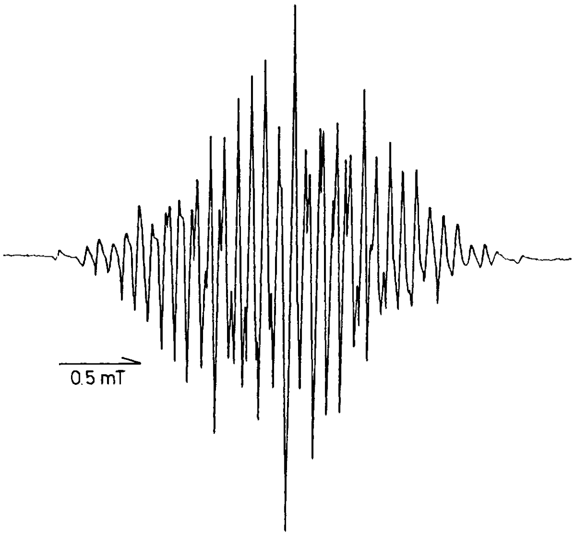


Figure 1. The observed e.s.r. spectrum for the radical anion $(\mathbf{1}^{-\cdot})$ formed by electrochemical reduction supported with TPAP in DME at −70 °C.

Table 1. The hyperfine splitting (h.f.s.) constants of the radical anion ($1^{-\bullet}$) and radical trianion ($1^{3-\bullet}$).

	Positions[a] and the h.f.s. constants/mT				
Radicals	1,10	2,9	3,8	4,7[b]	5,6
($1^{-\bullet}$), by elect.,[c]	0.320	0.160	0.010	0.237	0.428
with Na+,[d]	0.320	0.180	0.046	0.250	0.416
by calc.[e]	0.288	0.158	0.068	0.239	0.430
($1^{3-\bullet}$), with K+,[f]	0.570	0.120	0.512	0.030	~0
by calc.[g]	0.579	0.031	0.507	0.049	0.022

[a] The numbering is as shown in Figure 3. [b] The nitrogens. [c] At −70 °C in DME, supported with TPAP. [d] At −70 °C in DME, g = 2.0027. [e] The MO calculations are carried out by using parameters, $k_{CN} = k_{CC} = 1.0$, $h_N = 0.9$ in equations, $\alpha_x = \alpha_c + h_x\beta_{cc}$ and $\beta_{xy} = k_{xy}\beta_{cc}$, and $\lambda = 1.16$. The h.f.s. constants were computed by McConnel's equation, $a_i = Q\rho_i$ with parameters, $Q_H = |2.8|$, $Q_N = |1.9|$ mT. [f] At room temp. in DME, g = 2.0027. [g] The MO calculations are carried out using parameters, $k_{CN} = 1.5$, $k_{CC} = 1.0$, $h_N = 3.5$, $h_{C_3} = h_{C_5} = h_{C_6} = h_{C_8} = -0.1$ in the above equations, and $\lambda = 1.2$. Q values are the same as the values mentioned before.

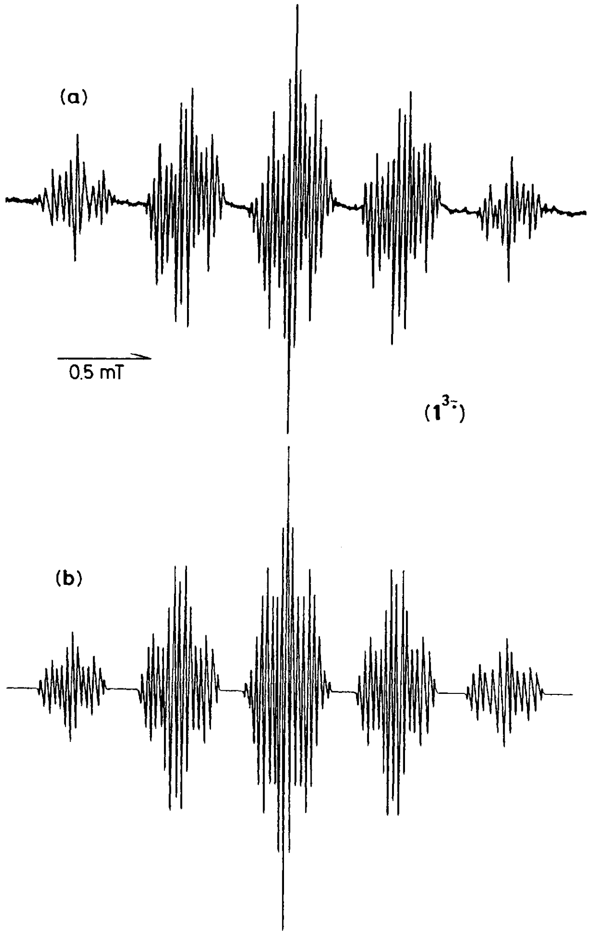
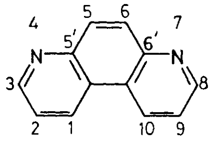


Figure 2. (a) The observed e.s.r. spectrum for the radical trianion ($1^{3-\bullet}$) formed by potassium metal-reduction of (**1**) in DME at room temperature and (b) its simulated spectrum.

estimated to be −2.10, −2.32, and −2.62 V *vs.* normal hydrogen electrode (NHE). This result indicates that the next lowest unoccupied molecular orbital (NLUMO) of (**1**) is very close to the lowest unoccupied molecular orbital (LUMO) and the trianion radical of (**1**), in which the NLUMO is singly occupied, is generated readily below −2.62 V. Scheme 1 summarizes the possible species formed by the electrochemical reduction with estimated $E_{1/2}$.



(**1**)

Figure 3

The e.s.r. spectra of the paramagnetic species generated by electrochemical and alkali metal reductions of (**1**) were observed in 1,2-dimethoxyethane (DME) in order to verify Scheme 1. The e.s.r. spectrum of the radical anion ($1^{-\bullet}$) formed by electrochemical reduction is shown in Figure 1. This spectrum could be simulated by the hyperfine splitting (h.f.s.) constants listed in Table 1. At any controlled potential available we could not obtain other radical species even at −70 °C. The reduction of (**1**) by sodium at −70 °C also showed a spectrum similar to Figure 1. However, the reduction by sodium at room temperature readily produced a second radical species, which led to a complicated spectrum owing to the superposition of the spectrum onto that of ($1^{-\bullet}$). On the other hand, the radical species produced by potassium gave only a well-resolved spectrum corresponding to that due to the second radical at room temperature. This is shown in Figure 2(a). The hyperfine structure of this spectrum is quite different from that due to ($1^{-\bullet}$) (Figure 1). Its h.f.s. constants obtained by simulation [Figure 2(b)] are also listed in Table 1. This suggests that when potassium is used as reductant, (**1**) is directly reduced into ($1^{3-\bullet}$), owing to the ionization potential of potassium being lower than that of sodium.

The identification of the radical species produced was carried out with the help of McLachlan's MO calculation. The results of the calculated h.f.s. constants[7] using appropriate parameters are also listed in Table 1. The calculated h.f.s. constants of ($1^{-\bullet}$) and ($1^{3-\bullet}$) agreed nicely with the observed h.f.s. constants of the first and second radical, respectively. Taking into account the CV data mentioned before, one can conclude that the second radical is the radical trianion of (**1**).

It is a great surprise to observe the radical trianion of such a small molecule as (**1**) at room temperature. It is probably due to the closeness of the NLUMO to the LUMO by the substitution of the two nitrogens to the 4- and 7-positions in the phenanthrene framework, as was evidenced by the CV data.

The spin density distribution in the NLUMO is also of interest. The percentage of the densities on carbons at the 1-, 3-, 8-, and 10-positions can be as large at about 77%, which leads to the wide hyperfine structure of ($1^{3-\cdot}$) shown in Figure 2(a). According to the frontier MO theory,[8] this result indicates that these positions are very reactive compared to other positions. Detailed investigation of the reactivity of (**1**) is now under way.

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