© 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 1529—1531 (1986)

The Effect of Triple-Ion Formation on the Electron-Exchange Reaction Rate between Quinone and Semiquinone Anion Radical

Tsuyoshi Takiguchi,† Kosaku Suga,* and Shigeru Aoyagui
Department of Chemical Engineering, Tokyo Institute of Technology,
Ohokayama, Meguro-ku, Tokyo 152
(Received October 23, 1985)

The rate constant and activation parameters of electron-exchange reactions between duroquinone, *p*-benzoquinone and 2,5-di-*t*-butyl-*p*-benzoquinone and their respective semiquinone anions which form ion-pairs or triple-ions with Na^+ and K^+ were determined. The rate constants of triple-ions were smaller than those of corresponding ion-pairs; the rate constants of potassium ion pairs and triple-ions were larger than those of the corresponding sodium aggregates; and the rate constants of triple-ions decreased upon increasing the size of the substituent for quinone. These results were explained on the basis of a mechanism which is generally accepted for electron-exchange reactions of ion pairs of anion radicals.

Although a considerable amount of work concerning the rates of electron-exchange reactions between aromatic compounds and their anion radicals, forming ion pairs, have been published, few results have been reported for anion radicals forming triple-ions.[1] Szwarc et al. compared the rate constant of the electron-exchange reaction for a duroquinone (DQ)/duroquinone anion (DQ^-) ion-pair system with that for a DQ/DQ^- triple-ion system.[1] Their results, unfortunately, only showed that the conversion of the ion-pair into the triple-ion influenced the rate of the electron-exchange reaction very little.

In the present work, we report on systematic measurements of the rate constants and activation parameters of electron-exchange reactions between DQ, *p*-benzoquinone (BQ), and 2,5-di-*t*-butyl-*p*-benzoquinone (2,5-DBBQ) and their respective semiquinone anions which form ion pairs or triple-ions with Na^+ and K^+ ions. We also examine whether the mechanism is applicable to the case of triple-ions which is generally accepted for the electron exchange of ion-pairs of anion radicals.[2,3]

Experimental

BQ was purified by sublimation. Commercial 2,5-DBBQ, 2,6-DBBQ, DQ, and sodium tetraphenylborate (NaTPhB) were used as obtained. Potassium tetraphenylborate (KTPhB) was prepared by a double decomposition of NaTPhB and potassium chloride. Tetrahydrofuran (THF) was purified in the same way as previously described.[4] Semiquinone anion radicals (Q^-) were prepared in vacuo by reducing their parent molecules (Q) with an anthracene anion radical. Solutions of triple ions were prepared by adding a weighed amount of dry alkali metal tetraphenylborate into the solutions of Q^- ion pairs. The rate constants of electron-exchange reactions were determined from the broadening of ESR spectra peaks which did not overlap each other. When direct measurements of line widths were difficult because of overlapping, rate constants were determined by computer simulation using a modified Bloch equation. X-band ESR spectra were recorded on a JEOL FE3X1 ESR spectrometer equipped with a variable-temperature adapter.

Results and Discussion

In Figs. 1 and 2, as tentative examples, we show the ESR Spectra for solutions of sodium ion-pair of DQ^- ($DQ^- \cdot Na^+$) and the sodium triple-ion of DQ^- ($DQ^- \cdot Na_2^{2+}$) containing different amounts of DQ at room temperature. The parameters for the ESR spectra of ion pairs and triple-ions measured in this

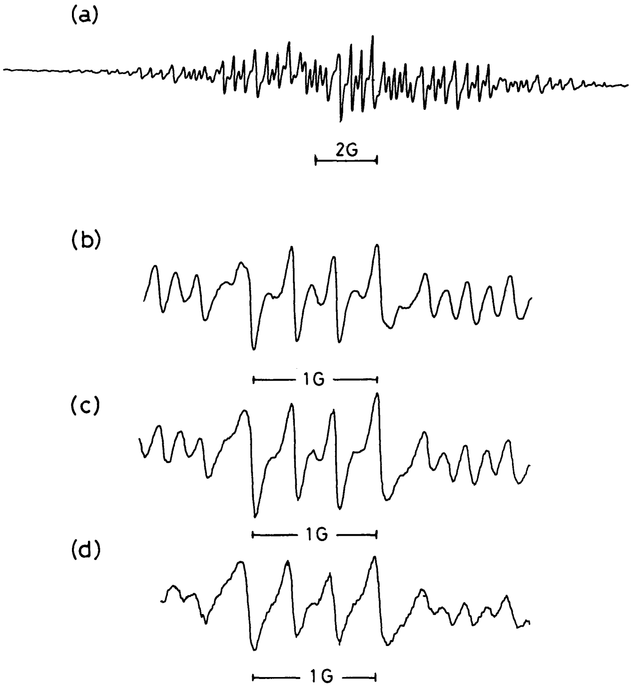

Fig. 1. ESR spectra for the ion-pair of DQ^- with sodium cation ($DQ^- \cdot Na^+$) in THF at 25 °C: (a) the whole spectrum; (b)—(d) central parts of the spectra in the presence of 0 mM, 0.67 mM, and 1.34 mM DQ respectively.

---

† Present address: Department of Electronic Chemistry, Graduate School of Nagatuta, Tokyo Institute of Technology, Nagatuta, Midori-ku, Yokohama 227.

experiment generally coincided with the values from the literatures.[5,6,7] In all cases, the line width of the ESR spectrum increased with the amounts of DQ as shown in Fig. 1 (b)—(d) and Fig. 2 (b)—(d). The rate constants and activation parameters obtained are shown in Table 1, where $Q^-\cdot M^+$ and $Q^-\cdot M_2^{2+}$ represent ion-pair and triple-ion, respectively. The free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation were determined by the use of Marcus' equation.

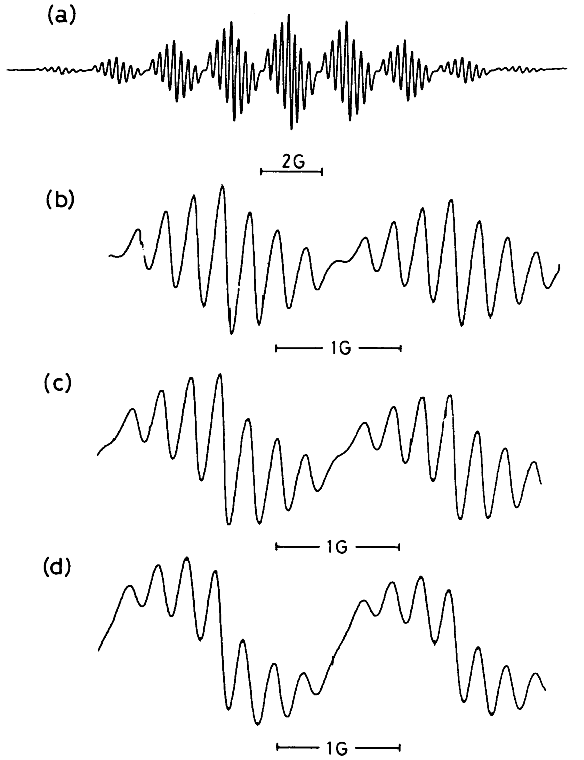

Fig. 2. ESR spectra for the triple-ion of DQ^- with sodium cations ($DQ^-\cdot Na_2^{2+}$) in THF containing 3.5 mM NaTPhB at 25 °C: (a) the whole spectrum; (b)—(d) the central parts of the spectra in the presence of 0 mM, 2.5 mM, and 5.0 mM DQ respectively.

The value of the rate constant for $DQ^-\cdot Na_2^{2+}/DQ$ listed in Table 1 agreed well with that reported by Szwarc et al.: $k=8.7\times10^7\ M^{-1}\ s^{-1}$.[1] However, they have only showed that the rate constant for $DQ^-\cdot Na_2^{2+}/DQ$ was little different from k for $DQ^-\cdot Na^+$ in contrast to our results.

The results listed in Table 1 have the following marked trends without exceptions: (a) The rate constants for triple-ions are smaller than those for ion-pairs; (b) the rate constants for potassium ion-pairs and triple-ions are larger than those for the corresponding sodium aggregates respectively; (c) ΔG^* of $Q^-\cdot M_2^{2+}$ increases with the size of substituents of Q, and this tendency is more prominent in $Q^-\cdot Na_2^{2+}$ than in $Q^-\cdot K_2^{2+}$.

On the other hand, the activation parameters of these electron-transfer reactions, except ΔG^*, have no clear trends like the rate constants or ΔG^*. At present, it is difficult to discuss the contribution of ΔH^* and $-T\Delta S^*$ to ΔG^* in these electron-transfer reactions. Therefore, we will now discuss the trends of the rate constants or ΔG^* described above.

These trends can be explained as follows. According to studies on the electron exchange reactions of ion pairs and triple-ions of anion radicals, it has been concluded that counter cations should transfer simultaneously with electrons.[1,2] Cations which form ion-pairs and triple-ions with semiquinone anions are surrounded by solvation shells and, therefore, a substantial expenditure of energy is needed to reorganize them to make an activated complex with a symmetric configuration before and after an electron-exchange reaction. This energy may contribute to the activation free energy for the

Table 1. Rate Constants and Activation Parameters of Electron-Exchange Reactions between Quinones and Semiquinone Anions in the Form of Ion-Pairs or Triple-Ions

Ion aggregate	$k\times10^{-8}$ a)	ΔG^*	ΔH^*	ΔS^*
	$dm^3\ mol^{-1}\ s^{-1}$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$	$J\ mol^{-1}\ K^{-1}$
$BQ^-\cdot Na_2^{2+}$	3.0	17	14	−10
$BQ^-\cdot K_2^{2+}$	5.3	15	6.2	−30
$DQ^-\cdot Na^+$	4.0	16	8.0	−26
$DQ^-\cdot Na_2^{2+}$	0.9	20	13	−23
$DQ^-\cdot K^+$	9.4	14	14	0
$DQ^-\cdot K_2^{+2}$	4.4	16	13	−11
2,5-DBBQ$^-\cdot Na^+$	0.62	21	16	−19
2,5-DBBQ$^-\cdot Na_2^{2+}$	0.01	30		
2,5-DBBQ$^-\cdot K^+$	1.3	19	13	−20
2,5-DBBQ$^-\cdot K_2^{2+}$	0.48	22	10	−30∼−40
2,6-DBBQ$^-\cdot Na^+$	0.43 b)	21		
2,6-DBBQ$^-\cdot K^+$	2.4	18	14	−12

a) At 25 °C. b) At 0 °C.

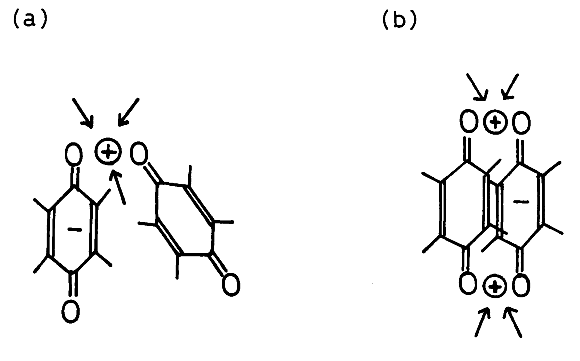

Fig. 3. Schematic illustration of activated complexes for the electron transfer reactions between quinone and its anion radical: (a) ion-pair; (b) triple-ion.

exchange reaction. When the cation is smaller, it is so much more strongly solvated that the energy barrier is higher and the rate of exchange reaction is smaller. Therefore, the rate constants of ion pairs or triple-ions with sodium ions are expected to be smaller than those for potassium aggregates. In the case of a triple-ion, where two counter ions interact with an anion, the reorganization energy of solvent molecules becomes larger than that in the case of an ion pair. Thus, trends (a) and (b) can be explained reasonably.

On the other hand, trend (c) can be interpreted as follows. The expected symmetric transition state involving semiquinone anion ion-pair might be schematically described as in Fig. 3(a). In this Figure, arrows indicate solvent orientations. It can be seen from this scheme that the relative angles between the both O–O axes and between the planes of two quinone molecules are variable. In contrast to the ion pair, in the case of triple-ion, the O–O axes of two quinone molecules must be parallel in symmetric transition state as illustrated schematically in Fig. 3(b). Therefore, as the size of substituents of Q become larger, the steric hindrance increases ΔG^{*} which is required to form the activated complex. This steric hindrance may be more prominent in $Q^{-}\cdot Na_2^{2+}/Q$ with smaller cation than in $Q^{-}\cdot K_2^{2+}/Q$. Thus, trend (c) also can be interpreted on the basis of the mechanism mentioned above, considering the steric hindrance in activation complexes.

These explanations indicate that the generally accepted mechanism of the electron-exchange reactions of ion-pairs of anion radicals can also be applied to the electron-exchange reactions of triple-ions.

We wish to thank Profs. Hiroshi Fukutomi and Hiroshi Tomiyasu for the use of facilities for the ESR measurement at The Research Laboratory for Nuclear Reactors in Tokyo Institute of Technology.

References

1) R. F. Adams, T. L. Staples, and M. Szwarc, *Chem. Phys. Lett.*, **5**, 474 (1970).

2) N. Hirota, "EPR Studies of Radical Anions in Solution," in "International Review of Science, Physical Chemistry Series II, Vol. 4, Magnetic Resonance," ed by C. A. McDowell, Butter-worth (1975), pp. 85—137.

3) M. Szwarc and J. Jagur-Grodzinski, "Ions and Ion Pairs in Electron Transfer Reactions of Radical Anions, Carbanions and Solvated Electrons," in "Ion and Ion Pairs in Organic Reactions," ed by M. Szwarc, John-Wiley Sons, (1974), Vol. 2, pp. 1—150.

4) K. Suga and S. Aoyagui, *Bull. Chem. Soc. Jpn.*, **46**, 755 (1973).

5) D. H. Chen, E. Warhurst, and A. Margaret Wilde, *Trans. Faraday Soc.*, **66**, 2561 (1967).

6) A. W. Rutter and E. Warhurst, *Trans. Faraday Soc.*, **64**, 2338 (1968).

7) M. P. Khakhar, B. S. Prabbananda, and M. R. Das, *J. Am. Chem. Soc.*, **89**, 3100 (1969).