

A Negative Temperature Dependence of the Electron Self-Exchange Rates of Zinc Porphyrin π Radical Cations

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In general the rate of any chemical reaction becomes faster with increasing reaction temperature, since an activation is required to reach the reaction transition state. However, there is a case where the rate of reaction becomes slower with increasing reaction temperature, provided that the reaction proceeds via an intermediate, the energy of which is lower than that of the reactant pair, and the energy difference between the reactant pair and the intermediate is larger than the activation energy from the intermediate. The first definitive case for a negative temperature dependence was reported by Kiselev and Miller who have shown that a negative activation enthalpy arises when the charge transfer (CT) complex formed between 9,10-dimethylantracene and tetracyanoethylene lies along the reaction pathway of the Diels–Alder reaction.¹ In such a case, the observed rate constant (k_{obs}) is given by

$$k_{\text{obs}} = k_1 K_{\text{CT}} \quad [\Delta H_{\text{obs}}^\ddagger = \Delta H_1^\ddagger (> 0) + \Delta H_{\text{CT}} (< 0)]$$

where k_1 is the intracomplex rate constant and K_{CT} is the formation constant of the CT complex. The necessary condition to observe a negative activation enthalpy for reactions involving CT complexes is that the heat of formation of the CT complex ($\Delta H_{\text{CT}} < 0$) is of greater magnitude than the activation enthalpy for the passage of the CT complex to the transition state ($\Delta H_1^\ddagger > 0$), that is, $-\Delta H_{\text{CT}} > \Delta H_1^\ddagger$.¹ Such a CT complex has been regarded as a key intermediate in a number of important chemical reactions.^{2–5} A negative temperature dependence has also been reported for the rates of hydride transfer reactions from 10-methyl-9,10-dihydroacridine to 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in chloroform to afford the negative activation enthalpy ($\Delta H_{\text{obs}}^\ddagger = -32 \text{ kJ mol}^{-1}$).^{6,7} However, there has been no report on a negative temperature effect caused by the presence of an intermediate for a simple electron-transfer reaction.⁸

Porphyrin π radical cations are known to play a crucial role in biological electron-transfer systems such as respiration and photosynthesis.⁹ We report herein a negative temperature dependence of the electron self-exchange between a zinc porphyrin π radical cation and the neutral form for the first time. Fine-tuning of the substituent on the porphyrin ring and the proper choice of the solvent has enabled us to observe negative activation enthalpies for the simple electron self-exchange reactions based on the ESR line width variation of the ESR spectra of zinc porphyrin radical cations.

The one-electron oxidation of ZnT(*t*-Bu)PP (T(*t*-Bu)PP²⁻ = 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin dianion, $5.0 \times 10^{-4} \text{ M}$) by one equivalent of Ru(bpy)₃³⁺ (bpy = 2,2'-bipyridine; $5.0 \times 10^{-4} \text{ M}$) results in quantitative formation of ZnT(*t*-Bu)PP^{•+}

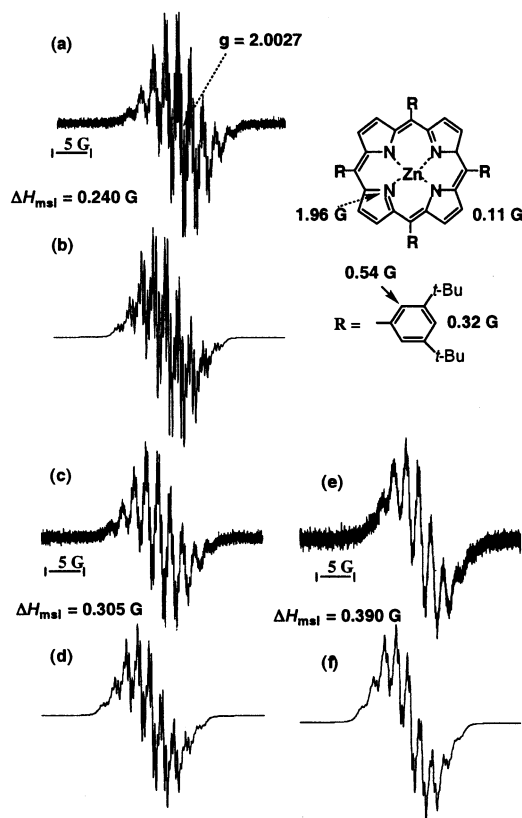


Figure 1. (a) ESR spectrum of ZnT(*t*-Bu)PP^{•+} ($5.0 \times 10^{-4} \text{ M}$) in toluene at 313 K and (b) the computer simulation spectrum ($\Delta H_{\text{msl}} = 0.240 \text{ G}$). (c) ESR spectrum of ZnT(*t*-Bu)PP^{•+} in the presence of ZnT(*t*-Bu)PP ($5.0 \times 10^{-4} \text{ M}$) in toluene at 313 K and (d) the computer simulated spectrum ($\Delta H_{\text{msl}} = 0.305 \text{ G}$). (e) ESR spectrum of ZnT(*t*-Bu)PP^{•+} in the presence of ZnT(*t*-Bu)PP ($5.0 \times 10^{-4} \text{ M}$) in toluene at 233 K and (f) the computer simulated spectrum ($\Delta H_{\text{msl}} = 0.390 \text{ G}$).

which is detected by ESR at 313 K as shown in Figure 1a. The hyperfine structure is well resolved as compared to the ESR spectra of porphyrin radical cations reported thus far.¹⁰ The hyperfine coupling constants (hfc) are determined by comparison of the observed spectrum with the computer simulated spectrum as shown in Figure 1b.¹¹ When an excess of ZnT(*t*-Bu)PP ($1.0 \times 10^{-3} \text{ M}$) is used for the oxidation with Ru(bpy)₃³⁺ ($5.0 \times 10^{-4} \text{ M}$) at 313 K, the ESR line width becomes broader than the spectrum obtained in the equimolar condition (Figure 1c,d). The line broadening results from the electron self-exchange between ZnT(*t*-Bu)PP^{•+} and ZnT(*t*-Bu)PP which is left in solution. To our surprise, the line width of the ESR signal of ZnT(*t*-Bu)PP^{•+} becomes broader as the temperature is decreased from 313 to 233 K (Figure 1e,f). This indicates that the electron self-exchange reaction becomes faster

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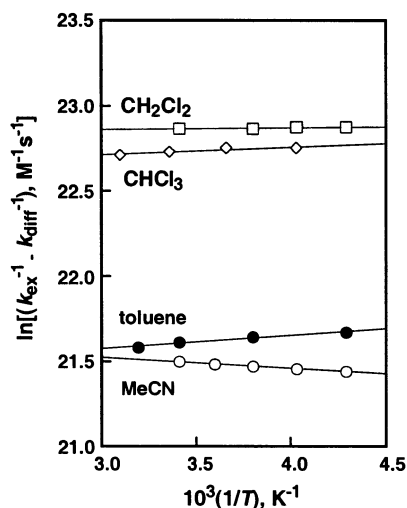


Figure 2. Arrhenius plots of electron self-exchange reaction between ZnT(*t*-Bu)PP⁺ and ZnT(*t*-Bu)PP in different solvents.

Table 1. Activation Parameters ($\Delta H_{\text{obs}}^\ddagger$ and $\Delta S_{\text{obs}}^\ddagger$) for the ZnT(*t*-Bu)PP/ZnT(*t*-Bu)PP⁺ and ZnTPP/ZnTPP⁺ Systems

	ZnT(<i>t</i> -Bu)PP ⁺		ZnTPP ⁺	
	$\Delta H_{\text{obs}}^\ddagger$ kJ mol ⁻¹	$\Delta S_{\text{obs}}^\ddagger$ kJ mol ⁻¹	$\Delta H_{\text{obs}}^\ddagger$ kJ mol ⁻¹	$\Delta S_{\text{obs}}^\ddagger$ kJ mol ⁻¹
MeCN	0.6	-30	2.2	-21
CH ₂ Cl ₂	-0.2	-14	0	-22
CHCl ₃	-1.0	-17	—	—
toluene	-0.9	-32	2.2	-24

^a The experimental error is $\pm 10\%$.

at a lower temperature. The rate constants (k_{ex}) of the electron exchange reactions between ZnT(*t*-Bu)PP⁺ and ZnT(*t*-Bu)PP were determined using eq 1,

$$k_{\text{ex}} = 1.52 \times 10^7 (\Delta H_{\text{msl}} - \Delta H_{\text{msl}}^0) / \{ (1 - P_1) [\text{ZnT}(\textit{t}\text{-Bu})\text{PP}] \} \quad (1)$$

where ΔH_{msl} and ΔH_{msl}^0 are the maximum slope line widths of the ESR spectra in the presence and absence of excess ZnT(*t*-Bu)PP, respectively, and P_1 is a statistical factor, which can be taken as nearly zero.¹² From the slopes of the linear plots of ΔH_{msl} and [ZnT(*t*-Bu)PP] are obtained the electron self-exchange rate constants (k_{ex}) in different solvents at various temperatures.¹³ The activation parameters are determined from the Arrhenius plots in Figure 2,^{14,15} where the positive slopes for the data in toluene, CH₂Cl₂, and CHCl₃ afford the negative activation enthalpies. In MeCN, however, a normal negative slope is obtained to afford the positive $\Delta H_{\text{obs}}^\ddagger$ value. The activation parameters were also determined for electron self-exchange between ZnTPP⁺ and ZnTPP (TPP²⁻ = tetraphenylporphyrin dianion, see Supporting Information, S4). The results are summarized in Table 1. The $\Delta H_{\text{obs}}^\ddagger$ values of the ZnTPP⁺/ZnTPP system are larger than those of the ZnT(*t*-Bu)PP⁺/ZnT(*t*-Bu)PP system.

The negative activation enthalpy indicates that electron self-exchange reaction proceeds via an intermediate, the energy of which is lower than that of the reactant pair, and the energy difference between the reactant pair and the intermediate is larger than the activation energy from the intermediate. In general, an electron-transfer reaction proceeds via a precursor complex formed between an electron donor and an acceptor.¹⁵ In the case of electron self-exchange, an electron donor is ZnT(*t*-Bu)PP which may form a charge-transfer π complex with an electron acceptor, ZnT(*t*-Bu)PP⁺.¹⁶ The formation of such a π complex may be sensitive to the

t-Bu substitution on the phenyl group of ZnTPP, affecting the $\Delta H_{\text{obs}}^\ddagger$ value. The negative $\Delta S_{\text{obs}}^\ddagger$ values in Table 1 are consistent with the complex formation prior to electron transfer. In the electron self-exchange reaction, there is no net change in solvation before and after the electron transfer, when the solvent reorganization energy of electron-transfer becomes smaller as the solvent polarity decreases.¹⁷ This may be the reason a negative activation enthalpy is observed for the ZnT(*t*-Bu)PP⁺/ZnT(*t*-Bu)PP system in less polar solvents such as CH₂Cl₂, CHCl₃, and toluene as compared to the case in MeCN (Table 1).

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Supporting Information Available: Data for electron self-exchange for the ZnT(*t*-Bu)PP/ZnT(*t*-Bu)PP⁺ and ZnTPP/ZnTPP⁺ systems (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036.
- (2) (a) Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39. (b) Rathore, R.; Kochi, J. K. *Adv. Phys. Org. Chem.* **2000**, *35*, 193. (c) Kim, J. H.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 4951.
- (3) (a) Fukuzumi, S. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1992; pp 67–175. (b) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.
- (4) Mulliken, R. S.; Person, W. B. *Molecular Complexes; A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.
- (5) (a) Chanon, M.; Tobe, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (b) Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193. (c) Jones, G., II. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, p 245.
- (6) Fukuzumi, S.; Ohkubo, K.; Tokuda, Y.; Suenobu, T. *J. Am. Chem. Soc.* **2000**, *122*, 4286.
- (7) (a) Zaman, K. M.; Yamamoto, S.; Nishimura, N.; Maruta, J.; Fukuzumi, S. *J. Am. Chem. Soc.* **1994**, *116*, 12099. (b) Yamamoto, S.; Sakurai, T.; Liu, Y. J.; Sueishi, Y. *Phys. Chem. Chem. Phys.* **1999**, *1*, 833.
- (8) For other examples of negative temperature effects, see: (a) Sergeev, G. B.; Serguchev, Yu. A.; Smirnov, V. V. *Russ. Chem. Rev.* **1973**, *42*, 697. (b) Kim, H.-B.; Kitamura, N.; Kawanishi, Y.; Tazuke, S. *J. Am. Chem. Soc.* **1987**, *109*, 2506.
- (9) (a) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26. (b) Fukuzumi, S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, 2000; Vol. 8, pp 115–151.
- (10) The ESR resolution of porphyrin π -radical cations is known to be affected by a variety of factors: the peripheral substitution, axial ligands, and solvents. See: (a) Felton, R. H.; Dolphin, D.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1969**, *91*, 196. (b) Ichimori, K.; Ohya-Nishiguchi, H.; Hirota, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2753. (c) Huber, M.; Galili, T.; Möbius, K.; Levanon, H. *Isr. J. Chem.* **1989**, *29*, 65. (d) Dave, P. C.; Srinivas, D. *Eur. J. Inorg. Chem.* **2000**, 447.
- (11) The well-resolved ESR spectrum enabled the determination of hfcs due to four nitrogens, eight β -pyrrole protons, eight *o*-phenyl protons, four *p*-phenyl protons as shown in Figure 1. For more accurate assignment of hfcs of ZnTPP⁺ by ENDOR, see ref 10c. It should be noted that the ESR resolution is highly dependent on the excess porphyrin concentration due to the rapid electron exchange.
- (12) (a) Chang, R. J. *Chem. Educ.* **1970**, *47*, 563. (b) Cheng, K. S.; Hirota, N. In *Investigation of Rates and Mechanisms of Reactions*; Hammes, G. G., Ed.; Wiley-Interscience: New York, 1974; Vol. VI, p 565.
- (13) The ΔH_{msl}^0 value in the absence of excess porphyrin slightly varies, depending on temperature and solvent (see Supporting Information S2). The same hyperfine coupling constants were used to fit well the ESR spectra using different ΔH_{msl} values irrespective of temperature or solvent. Thus, the observed line broadening due to electron self-exchange was in the slow-exchange region.¹² At each temperature, the $\Delta H_{\text{msl}} - \Delta H_{\text{msl}}^0$ value is plotted against excess porphyrin concentration (S3).
- (14) The diffusion is taken into account in the Arrhenius plot, based on the relation: $(k_{\text{ex}} - k_{\text{diff}})^{-1} = Z \exp(-\Delta G^\ddagger/RT)$, where k_{diff} is the diffusion rate constant and Z is the collision frequency.¹⁵
- (15) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; Wiley-VCH: New York, 1993.
- (16) No charge-transfer (CT) band between ZnT(*t*-Bu)PP⁺ and ZnT(*t*-Bu)PP was observed under the present experimental conditions.
- (17) Fukuzumi, S.; Ohkubo, K.; Suenobu, T.; Kato, K.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 8459.

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