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

Shunichi Fukuzumi,* Yoshito Endo, and Hiroshi Imahori[†]

Department of Material and Life Science, Graduate School of Engineering, CREST, JST,
Osaka University, Suita 565-0871, Japan

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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-dimethylanthracene 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

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

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 ($\Delta H_{CT} < 0$) 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, $-\Delta H_{CT} > \Delta H_1^{\ddagger}$.[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 ($\Delta H_{obs}^{\ddagger} = -32$ 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.

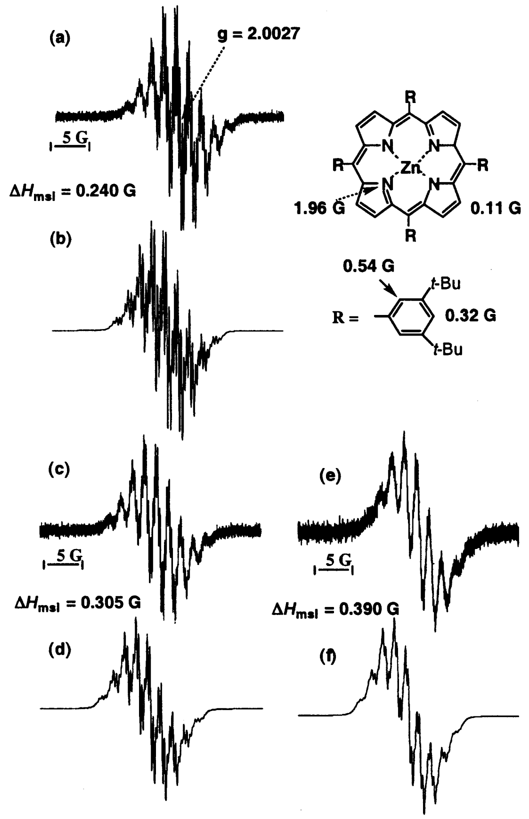

Figure 1. (a) ESR spectrum of ZnT(*t*-Bu)PP$^{\bullet+}$ (5.0×10^{-4} M) in toluene at 313 K and (b) the computer simulation spectrum ($\Delta H_{msl} = 0.240$ G). (c) ESR spectrum of ZnT(*t*-Bu)PP$^{\bullet+}$ in the presence of ZnT(*t*-Bu)PP (5.0×10^{-4} M) in toluene at 313 K and (d) the computer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

The one-electron oxidation of ZnT(*t*-Bu)PP (T(*t*-Bu)PP^{2-} = 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin dianion, 5.0×10^{-4} M) by one equivalent of Ru(bpy)$_3^{3+}$ (bpy = 2,2′-bipyridine: 5.0×10^{-4} M) results in quantitative formation of ZnT(*t*-Bu)PP$^{\bullet+}$ 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 (1.0×10^{-3} M) is used for the oxidation with Ru(bpy)$_3^{3+}$ (5.0×10^{-4} 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$^{\bullet+}$ 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$^{\bullet+}$ 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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* To whom correspondence should be addressed: Fax: +81(0)6-6879-7370. E-mail fukuzumi@ap.chem.eng.osaka-u.ac.jp.
[†] Present address: Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan.

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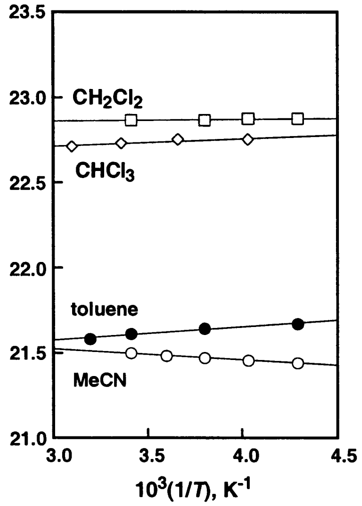

Figure 2. Arrhenius plots of electron self-exchange reaction between ZnT(*t*-Bu)PP$^{\bullet+}$ and ZnT(*t*-Bu)PP in different solvents.

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

	ZnT(*t*-Bu)PP$^{\bullet+}$		ZnTPP$^{\bullet+}$	
	$\Delta H^{\ddagger}_{obs}$[a] kJ mol^{-1}	$\Delta S^{\ddagger}_{obs}$[a] kJ mol^{-1}	$\Delta H^{\ddagger}_{obs}$[a] kJ mol^{-1}	$\Delta S^{\ddagger}_{obs}$[a] kJ mol^{-1}
MeCN	0.6	−30	2.2	−21
CH_2Cl_2	−0.2	−14	0	−22
$CHCl_3$	−1.0	−17	–	–
toluene	−0.9	−32	2.2	−24

[a] The experimental error is ±10%.

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

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

where ΔH_{msl} and ΔH^0_{msl} are the maximum slope line widths of the ESR spectra in the presence and absence of excess ZnT(*t*-Bu)PP, respectively, and P_i 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, CH_2Cl_2, and $CHCl_3$ afford the negative activation enthalpies. In MeCN, however, a normal negative slope is obtained to afford the positive $\Delta H^{\ddagger}_{obs}$ value. The activation parameters were also determined for electron self-exchange between ZnTPP$^{\bullet+}$ and ZnTPP (TPP^{2-} = tetraphenylporphyrin dianion, see Supporting Information, S4). The results are summarized in Table 1. The $\Delta H^{\ddagger}_{obs}$ values of the ZnTPP$^{\bullet+}$/ZnTPP system are larger than those of the ZnT(*t*-Bu)PP$^{\bullet+}$/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$^{\bullet+}$.[16] The formation of such a π complex may be sensitive to the *t*-Bu substitution on the phenyl group of ZnTPP, affecting the $\Delta H^{\ddagger}_{obs}$ value. The negative $\Delta S^{\ddagger}_{obs}$ 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$^{\bullet+}$/ZnT(*t*-Bu)PP system in less polar solvents such as CH_2Cl_2, $CHCl_3$, 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$^{\bullet+}$ and ZnTPP/ZnTPP$^{\bullet+}$ systems (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The diffusion is taken into account in the Arrhenius plot, based on the relation: $(k_{ex}^{-1} - k_{diff}^{-1})^{-1} = Z \exp(-\Delta G^{\ddagger}/RT)$, where k_{diff} is the diffusion rate constant and Z is the collision frequency.[15]
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