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Characteristic Activity Parameters of Electron Donors and Electron Acceptors

Jin-Ye Zhang, Li-Li Wang, and Xiao-Qing Zhu*

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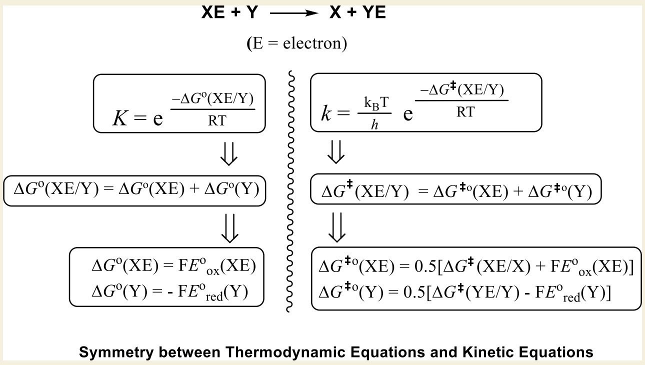

Symmetry between Thermodynamic Equations and Kinetic Equations

ABSTRACT: It is well-known that for an electron transfer reaction, the electron-donating ability of electron donors and the electron-accepting ability of electron acceptors can be quantitatively described by the oxidation potential of electron donors and the reduction potential of electron acceptors. However, for an electron transfer reaction, the electron-donating activity of electron donors and the electron-accepting activity of electron acceptors cannot be quantitatively described by a characteristic parameter of electron donors and a characteristic parameter of electron acceptors till now. In this paper, a characteristic activity parameter of electron donors and electron acceptors named as their thermo-kinetic parameter is proposed to quantify the electron-donating activity of electron donors and the electron-accepting activity of electron acceptors in electron transfer reactions. At the same time, the thermo-kinetic parameter values of 70 well-known electron donors and the corresponding 70 conjugated electron acceptors in acetonitrile at 298 K are determined. The activation free energies of 4900 typical electron transfer reactions in acetonitrile at 298 K are estimated according to the thermo-kinetic parameter values of 70 electron donors and 70 conjugated electron acceptors, and the estimated results have received good verification of the corresponding independent experimental measurements. The physical meaning of the thermo-kinetic parameter is examined. The relationship of the thermo-kinetic parameter with the corresponding redox potential as well as the relationship of the activation free energy with the corresponding thermodynamic driving force of electron transfer reactions is examined. The results show that the observed relationships between the thermo-kinetic parameters and the redox potentials as well as the observed relationships between the activation free energy and the thermodynamic driving force depend on the choice of electron donors and electron acceptors as well as the electron transfer reactions. The greatest contribution of this paper is to realize the symmetry and unification of kinetic equations and the corresponding thermodynamic equations of electron transfer reactions.

KEYWORDS: *electron transfer reaction, activity of reactant, activity of oxidant, thermo-kinetic parameter, activation free energy, kinetic equation*

■ INTRODUCTION

Electron transfer (ET) reaction (eq 1) is the most basic chemical reaction and exists widely in nature. Since the electron transfer process plays the core role in material metabolism, energy conversion, photosynthesis, biosynthesis and transformation, and many other processes, scientists in many fields such as physics, chemistry, biology, power source, and so on have all paid much more attention to the issues on the electron transfer process.[1−20] Among the many important issues on the electron transfer process, one of the most core issues is how to quantitatively predict the activation free energy $\Delta G^{\neq}$(XE/Y) of electron transfer reactions (eq 1). Although quite a lot of empirical and theoretical equations have been proposed by some scientists such as London−Eyring−Polanyi−Sato (LEPS),[21−23] Johnston and Parr,[24,25] Marcus,[26,27] Murdoch,[28] Rehm and Weller,[29] Agmon and Levine,[30] Bell,[31] le Noble,[32] Lewis,[33,34] Kurz,[35] Thornton,[36] Zavitsas,[37,38] and Ahrland−Chatt−Davies−Williams[39] to quantitatively predict the activation free energy of electron transfer reactions in terms of some parameters of electron transfer reactions, none[40] can be used to quantitatively estimate the activation free energy of electron transfer reactions based on only one characteristic parameter of electron donors and one characteristic parameter of electron acceptors as the calculation of the thermodynamic driving forces ΔG^{0}(XE/Y) of electron transfer reactions (eq 1), which can be calculated based on only one characteristic parameter of electron donors and one character-

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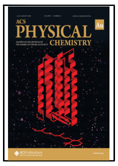

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istic parameter of electron acceptors (i.e., the oxidation potential of electron donors and the reduction potential of electron acceptors). The fundamental reason is that no suitable characteristic parameter of electron donors and electron acceptors can be found to quantify the electron-donating activity of electron donors (i.e., an actual ability of electron donors to donate electrons in an ET reaction, which directly determines the rate of electron transfer) and the electron-accepting activity of electron acceptors (i.e., an actual ability of electron acceptors to accept electrons in an ET reaction, which directly determines the rate of electron transfer) in electron transfer reactions till now. In this paper, we report a new characteristic parameter of electron donors and a new characteristic parameter of electron acceptors named as their thermo-kinetic parameters. The thermo-kinetic parameters of electron donors and electron acceptors can be used not only to quantify the electron-donating activity of the electron donor and the electron-accepting activity of the electron acceptor in electron transfer reactions but also to make the activation free energy of electron transfer reactions as their thermodynamic driving force can be calculated using only one characteristic parameter of electron donors and one characteristic parameter of electron acceptors.

$$\mathrm{XE} + \mathrm{Y} \rightarrow \mathrm{X} + \mathrm{YE} \quad (\mathrm{E} = \text{electron}) \tag{1}$$

$$\Delta G^0(\mathrm{XE/Y}) = \mathrm{F}E_{\mathrm{ox}}(\mathrm{XE}) - \mathrm{F}E_{\mathrm{red}}(\mathrm{Y})$$
$$\Delta G^{\neq}(\mathrm{XE/Y}) = f(\mathrm{XE}) + f(\mathrm{Y}) \tag{2}$$

RESULTS AND DISCUSSION

Definition of Thermo-Kinetic Parameters of Electron Donors and Electron Acceptors

To predict the activation free energy of a chemical reaction based on only one characteristic parameter of reactants, in our previous papers,[41,42] we examined the free energy change of reactants when the atom or atom group (L) transfer from XL to Y to form X and YL (eq 3). If the free energy change of the two interacting reactants (XL and Y) during L-transfer from XL to Y can be described using two Morse free energy curves and the intrinsic barrier of the L-transfer reaction $\Delta G^{\neq}{}_{\mathrm{o}}(\mathrm{XL/Y})$ (i.e., the activation free energy of the L-transfer reaction when thermodynamic driving force of the reaction is zero) is assumed to be equal to the average value of the activation free energies of the corresponding two self-exchange reactions for the two reactants: $\Delta G^{\neq}(\mathrm{XL/X})$ for XL + X → X + XL and $\Delta G^{\neq}(\mathrm{YL/Y})$ for Y + YL → YL + Y (eq 4), a new kinetic equation (eq 5) can be formed according to the classical transition-state theory. In eq 5, $\Delta G^{\neq}(\mathrm{XL/Y})$ is the activation free energy of L-transfer reactions; $\Delta G^0(\mathrm{XL/Y})$ is the free energy change of L-transfer reactions; $\Delta G^{\neq}(\mathrm{XL/X})$ is the activation free energy of the self-exchange reaction of XL with X (XL + X → X + XL); and $\Delta G^{\neq}(\mathrm{YL/Y})$ is the activation free energy of the self-exchange reaction of Y with YL (Y + YL→ YL+ Y). Because the free energy change of L-transfer reactions, $\Delta G^0(\mathrm{XL/Y})$, is equal to the addition of the free energy change of reactant XL releasing L $\Delta G^0(\mathrm{XL})$ and the free energy change of reactant Y accepting L $\Delta G^0(\mathrm{Y})$ (eq 6), eq 7 can be derived from eq 5 when $\Delta G^0(\mathrm{XL/Y})$ is replaced by $\Delta G^0(\mathrm{XL}) + \Delta G^0(\mathrm{Y})$.[23] In eq 7, $\Delta G^{\neq 0}(\mathrm{XL})$ is equal to the average of the activation free energy of the self-exchange reaction of XL with X (XL + X → X + XL), $\Delta G^{\neq}(\mathrm{XL/X})$, and the molar free energy change of XL releasing L, $\Delta G^0(\mathrm{XL})$ (eq 8); $\Delta G^{\neq 0}(\mathrm{Y})$ is equal to the average of activation free energy of self-reaction of Y with YL (YL + Y → Y + YL) $\Delta G^{\neq}(\mathrm{YL/Y})$ and the molar free energy change of Y accepting L $\Delta G^0(\mathrm{Y})$ (eq 9). Since both $\Delta G^{\neq}(\mathrm{XL/X})$ and $\Delta G^0(\mathrm{XL})$ in eq 8 are the characteristic energetic parameters of XL, $\Delta G^{\neq 0}(\mathrm{XL})$ is also a characteristic energetic parameter of XL. In other words, the value of $\Delta G^{\neq 0}(\mathrm{XL})$ is independent of the change of the reaction partner (Y). In addition, since $\Delta G^0(\mathrm{XL})$ is a thermodynamic parameter of XL and $\Delta G^{\neq}(\mathrm{XL/X})$ is a kinetic parameter of XL, $\Delta G^{\neq 0}(\mathrm{XL})$ is named as the thermo-kinetic parameter of XL.[43] Likewise, $\Delta G^{\neq 0}(\mathrm{Y})$ in eq 9 is a characteristic energetic parameter of the reactant Y and named as the thermo-kinetic parameter of Y.[43] Since the activation free energy of L-transfer reactions, $\Delta G^{\neq}(\mathrm{XL/Y})$, is determined only by $\Delta G^{\neq 0}(\mathrm{XL})$ and $\Delta G^{\neq 0}(\mathrm{Y})$, it is clear that the $\Delta G^{\neq 0}(\mathrm{XL})$ value can be used as a quantitative scale of the activity of XL in the reaction, and the $\Delta G^{\neq 0}(\mathrm{Y})$ value can be used as a quantitative scale of the activity of Y in the reaction

$$\mathrm{XL} + \mathrm{Y} \rightarrow \mathrm{X} + \mathrm{YL}$$
$$(\mathrm{L} = \mathrm{H}^-, \mathrm{H}^\bullet, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{Br}^\bullet, \mathrm{CN}^-, \mathrm{NO}, \mathrm{NO}^+, \cdots) \tag{3}$$

If

$$\Delta G^{\neq}{}_{\mathrm{o}}(\mathrm{XL/Y}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{XL/X}) + \Delta G^{\neq}(\mathrm{YL/Y})] \tag{4}$$

$$\Delta G^{\neq}(\mathrm{XL/Y}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{XL/X}) + \Delta G^{\neq}(\mathrm{YL/Y})] + \frac{1}{2}\Delta G^0(\mathrm{XL/Y}) \tag{5}$$

$$\Delta G^0(\mathrm{XL/Y}) = \Delta G^0(\mathrm{XL}) + \Delta G^0(\mathrm{Y}) \tag{6}$$

$$\Delta G^{\neq}(\mathrm{XL/Y}) = \Delta G^{\neq 0}(\mathrm{XL}) + \Delta G^{\neq 0}(\mathrm{Y}) \tag{7}$$

In eq 7

$$\Delta G^{\neq 0}(\mathrm{XL}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{XL/X}) + \Delta G^0(\mathrm{XL})] \tag{8}$$

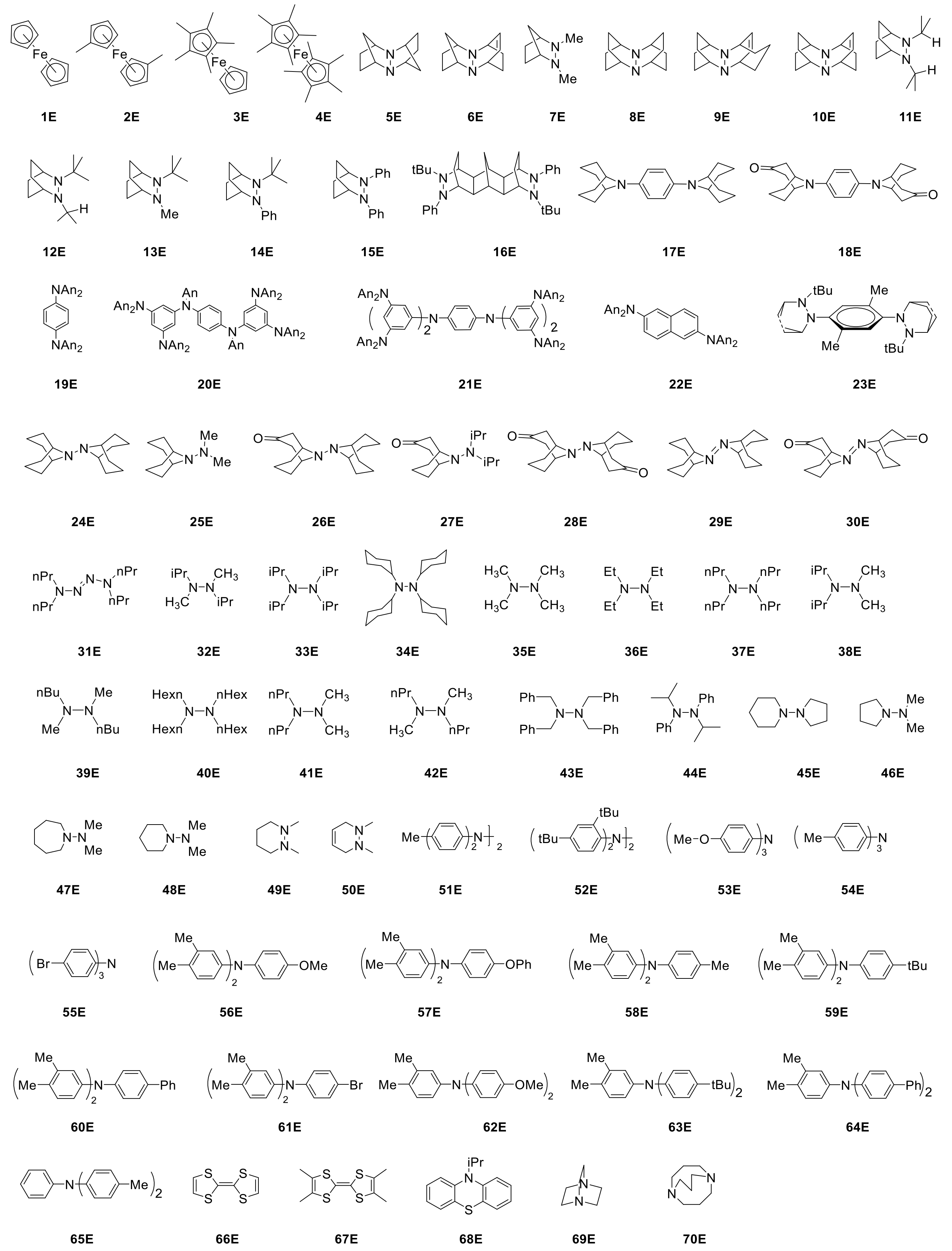
$$\Delta G^{\neq 0}(\mathrm{Y}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{YL/Y}) + \Delta G^0(\mathrm{Y})] \tag{9}$$

If eqs 7 and 6 are compared, it is clear that like the thermodynamic driving force of the L-transfer reaction $\Delta G^0(\mathrm{XL/Y})$, the activation free energy $\Delta G^{\neq}(\mathrm{XL/Y})$ of the L-transfer reaction can be calculated also according to one characteristic parameter of the L-donor (XL) and one characteristic parameter of the L-acceptor (Y) in the L-transfer reaction.

The validity of eq 7 to estimate the activation free energy of L-transfer reactions using the thermo-kinetic parameters of reactants has been extensively verified by successful predictions of the activation free energies of hydrogen atom transfer reactions,[43−48] hydride transfer reactions,[41,49−53] and kinetic isotope effect (KIE) values of hydride transfer reactions[54] in acetonitrile at 298 K.

For electron transfer reactions (eq 1), eq 7 is of validity also, because L in eq 3 can be regarded as an electron and eqs 8 and 9 can be replaced by eqs 10 and 11, respectively. In eq 10, $\mathrm{F}E_{\mathrm{ox}}(\mathrm{XE})$ is the molar free energy change of electron donor XE releasing E (E = electron). In eq 11, $-\mathrm{F}E_{\mathrm{red}}(\mathrm{Y})$ is the molar free energy change of electron acceptor Y accepting E. Since $\Delta G^{\neq}(\mathrm{XE/X})$ and $\mathrm{F}E_{\mathrm{ox}}(\mathrm{XE})$ are all of the characteristic

Scheme 1. Structure and Marks of 70 Electron Donors Examined in This Work (1E−70E)



energetic parameters of XE, $\Delta G^{\neq 0}(\mathrm{XE})$ is also a characteristic energetic parameter of the electron donor (XE). Likewise, $\Delta G^{\neq 0}(\mathrm{Y})$ is also a characteristic energetic parameter of the electron acceptor (Y). Since the activation free energy of electron transfer reactions, $\Delta G^{\neq}(\mathrm{XE/Y})$, is determined only by $\Delta G^{\neq 0}(\mathrm{XE})$ and $\Delta G^{\neq 0}(\mathrm{Y})$, the values of $\Delta G^{\neq 0}(\mathrm{XE})$ and $\Delta G^{\neq 0}(\mathrm{Y})$ can be used as a quantitative scale of the electron-releasing activity of XE and a quantitative scale of the electron-accepting activity of Y, respectively. It is clear that as long as the thermo-kinetic parameter values of electron donors and electron acceptors are available, the activation free energy of electron transfer reactions can be directly calculated in terms of the thermo-kinetic parameter values of the two reactants using eq 7.

The definition of the thermo-kinetic parameters of the electron donor (XE) and electron acceptor (Y) is as follows

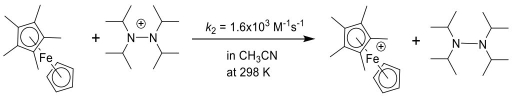
$$\Delta G^{\neq 0}(\mathrm{XE}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{XE/X}) + \mathrm{F}E_{\mathrm{ox}}(\mathrm{XE})] \tag{10}$$

$$\Delta G^{\neq 0}(\mathrm{Y}) = \frac{1}{2}[\Delta G^{\neq}(\mathrm{YE/Y}) - \mathrm{F}E_{\mathrm{red}}(\mathrm{Y})] \tag{11}$$

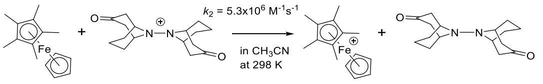
Method to Determine Thermo-Kinetic Parameters

According to the definition formula of the thermo-kinetic parameter of electron donors, $\Delta G^{\neq 0}(\mathrm{XE})$ (eq 10), $\Delta G^{\neq 0}(\mathrm{XE})$ value is derived from $\Delta G^{\neq}(\mathrm{XE/X})$ and $\mathrm{F}E_{\mathrm{ox}}(\mathrm{XE})$ values. For $E_{\mathrm{ox}}(\mathrm{XE})$ value, we can obtain it easily by direct experimental measurement using CV and/or OSWV methods, but for $\Delta G^{\neq}(\mathrm{XE/X})$ value, its direct determination is difficult because no signal change from reactants to products can be found during the self-reaction (XE + X → X + XE). This case indicates that both the thermo-kinetic parameter values of electron donors and electron acceptors cannot be obtained according to their definition formula. However, for a cross-electron-transfer reaction of XE with Y (XE + Y → X + YE, here X ≠ Y), if $\Delta G^{\neq 0}(\mathrm{XE})$ or $\Delta G^{\neq 0}(\mathrm{Y})$ is known, $\Delta G^{\neq 0}(\mathrm{Y})$ or $\Delta G^{\neq 0}(\mathrm{XE})$ can be derived from $\Delta G^{\neq}(\mathrm{XE/Y})$ according to eq 7 because the signal of reactants is generally different from that of products for cross-electron-transfer reactions. Obviously, if this method is used repeatedly, the thermo-kinetic parameter values of various electron donors XE and various electron acceptors Y can be measured. Therefore, to build the $\Delta G^{\neq 0}(\mathrm{XE})$ database of electron donors and $\Delta G^{\neq 0}(\mathrm{Y})$ database of electron acceptors, the first and key task is to find one suitable electron donor (XE) or one suitable electron acceptor (Y) whose thermo-kinetic parameter value can be obtained.

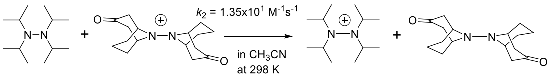
Although the thermo-kinetic parameter values of electron donors and electron acceptors cannot be derived from the definition formula, the thermo-kinetic parameter values of the electron donors and electron acceptors can be derived from the activation energies of the three related cross-electron-transfer reactions using the "four equations combined solution" method.[41,43,54] In this work, we choose **3E**, **28E**, and **33E** as well as their corresponding conjugated cations (**3**, **28**, and **33**) (Scheme 1) as electron donors and electron acceptors to construct three different cross-electron-transfer reactions (eqs 12−14). According to the three reaction equations (eqs 12−14), eqs 15−17 can be derived from eq 7. In eqs 15−17, $\Delta G^{\neq}(\mathbf{3E/33})$, $\Delta G^{\neq}(\mathbf{3E/28})$, and $\Delta G^{\neq}(\mathbf{33E/28})$ are the activation free energies of the three cross-electron-transfer reactions (eqs 12−14), the values in acetonitrile at 298 K can be derived from the corresponding known second-order rate constants in acetonitrile at 298 K ($k_2 = 1.60 \times 10^3$, 5.30×10^6, and 1.35×10^1 $\mathrm{M^{-1}\,s^{-1}}$ for the reactions of eqs 12, 13, and 14, respectively)[55] using the Eyring equation. The detailed result is that $\Delta G^{\neq}(\mathbf{3E/33}) = 13.08$ kcal mol^{-1}, $\Delta G^{\neq}(\mathbf{3E/28}) = 8.28$ kcal mol^{-1}, and $\Delta G^{\neq}(\mathbf{33E/28}) = 15.9$ kcal mol^{-1}. $\Delta G^{\neq 0}(\mathbf{3E})$, $\Delta G^{\neq 0}(\mathbf{33E})$, $\Delta G^{\neq 0}(\mathbf{28})$, and $\Delta G^{\neq 0}(\mathbf{33})$ in the three equations (eqs 15−17) are the thermo-kinetic parameters of the electron donors **3E** and **33E** and the electron acceptors **28** and **33**, respectively. Their values are all unknown. Since there are four unknown parameters in the three equations (eqs 15−17), the values of the four unknown parameters cannot be obtained through the combined solution of the three equations (eqs 15−17). However, for the self-exchange electron transfer reaction of **33E** with **33** (**33E** + **33** → **33** + **33E**), if eq 10 is subtracted from eq 11, eq 18 can be obtained from eqs 10 and 11 [note: $E_{\mathrm{ox}}(\mathrm{XE}) = E_{\mathrm{red}}(\mathrm{X})$]. Since $E_{\mathrm{ox}}(\mathbf{33E})$ in eq 18 is known (2.16 V vs $\mathrm{H^{+/0}}$),[56] the values of $\Delta G^{\neq 0}(\mathbf{3E})$, $\Delta G^{\neq 0}(\mathbf{33E})$, $\Delta G^{\neq 0}(\mathbf{28})$, and $\Delta G^{\neq 0}(\mathbf{33})$ in the three equations (eqs 15−17) can be obtained through the combined solution of the four equations (eqs 15−18). The result is that $\Delta G^{\neq 0}(\mathbf{3E}) = 27.66$ kcal mol^{-1}, $\Delta G^{\neq 0}(\mathbf{33E}) = 34.86$ kcal mol^{-1}, $\Delta G^{\neq 0}(\mathbf{33}) = -19.06$ kcal mol^{-1}, and $\Delta G^{\neq 0}(\mathbf{28}) = -19.38$ kcal mol^{-1}.



3E **33** **3** **33E** (12)



3E **28** **3** **28E** (13)



33E **28** **33** **28E** (14)

$$\Delta G^{\neq}(\mathbf{3E/33}) = \Delta G^{\neq 0}(\mathbf{3E}) + \Delta G^{\neq 0}(\mathbf{33}) \tag{15}$$

$$\Delta G^{\neq}(\mathbf{3E/28}) = \Delta G^{\neq 0}(\mathbf{3E}) + \Delta G^{\neq 0}(\mathbf{28}) \tag{16}$$

$$\Delta G^{\neq}(\mathbf{33E/28}) = \Delta G^{\neq 0}(\mathbf{33E}) + \Delta G^{\neq 0}(\mathbf{28}) \tag{17}$$

$$\Delta G^{\neq 0}(\mathbf{33E}) - \Delta G^{\neq 0}(\mathbf{33}) = \Delta G^{0}(\mathbf{33E}) \tag{18}$$

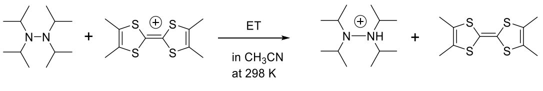
Since the thermo-kinetic parameter values of the electron donors **3E** (27.66 kcal mol^{-1}) and **33E** (34.86 kcal mol^{-1}) and the thermo-kinetic parameter values of the electron acceptors **33** (−19.06 kcal/mol) and **28** (−19.38 kcal mol^{-1}) in acetonitrile at 298 K have been obtained, it is not difficult to get the $\Delta G^{\neq 0}(\mathrm{Y})$ value of any other electron acceptor (**Y**) and the $\Delta G^{\neq 0}(\mathrm{XE})$ value of any other electron donor (**XE**) in acetonitrile at 298 K using eq 7 by constructing a suitable cross-electron-transfer reaction of **3E** or **33E** with an electron acceptor **Y** (**3E** or **33E** + **Y** → **3** or **33** + **YE**) or a suitable cross-electron-transfer reaction of **33** or **28** with an electron donor **XE** (**33** or **28** + **XE** → **33E** or **28E** + **X**). The electron transfer reaction of **33E** with the cation of 4,4′,5,5′-tetramethyl-2,2′-bi(1,3-dithiolylidene) (**67**) (eq 19)[57] and the electron transfer reaction of **28** with ferrocene (**1E**) (eq 20)[55] are two examples. Since the second-order rate constant (k_2) of the reaction (eq 19) in acetonitrile at 298 K is 5.20×10^5 $\mathrm{M^{-1}\,s^{-1}}$,[57] and the second-order rate constant (k_2) of the reaction (eq 20) in acetonitrile at 298 K is 4.80×10^4 $\mathrm{M^{-1}\,s^{-1}}$,[57] the activation free energy of the reaction (eq 19) in acetonitrile at 298 K is 9.65 kcal mol^{-1} and the activation free energy of the reaction (eq 20) is 11.06 kcal mol^{-1} using Eyring equation. In addition, since $\Delta G^{\neq 0}(\mathbf{33E}) = 34.86$ kcal mol^{-1}

Table 1. Thermo-Kinetic Parameter Values of 70 XE and 70 X, Molar Free Energy Changes of 70 XE Releasing Electrons and 70 X Accepting Electrons Together with Activation Free Energies of 70 Self-Reactions in Acetonitrile at 298 K (kcal mol^{-1})

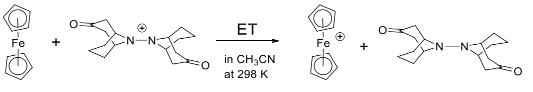
electron donor (XE)	XE		X		
	$\Delta G^0(XE)$[a]	$\Delta G^{\neq 0}(XE)$	$\Delta G^0(X)$[a]	$\Delta G^{\neq 0}(X)$	$\Delta G^{\neq}(XE/X)$[b]
1E	52.97	30.44	−52.97	−22.53	7.91
2E	50.34	28.86	−50.34	−21.48	7.38
3E	46.72	27.66	−46.72	−19.06	8.60
4E	41.35	24.63	−41.35	−16.71	7.92
5E	44.09	28.73	−44.09	−15.36	13.37
6E	45.20	29.65	−45.20	−15.55	14.10
7E	47.32	32.47	−47.32	−14.85	17.62
8E	31.64	24.52	−31.64	−7.12	17.40
9E	36.99	25.90	−36.99	−11.09	14.81
10E	38.30	26.51	−38.30	−11.79	14.72
11E	45.70	30.00	−45.70	−15.71	14.29
12E	41.55	28.45	−41.55	−13.11	15.34
13E	46.40	31.42	−46.40	−14.98	16.44
14E	49.86	31.30	−49.86	−18.56	12.74
15E	54.93	33.12	−54.93	−21.81	11.31
16E	48.13	30.06	−48.13	−18.07	11.99
17E	44.32	25.63	−44.32	−18.69	6.94
18E	50.55	28.78	−50.55	−21.77	7.01
19E	51.93	28.54	−51.93	−23.39	5.15
20E	55.16	30.26	−55.16	−24.90	5.36
21E	55.62	31.41	−55.62	−24.21	7.20
22E	54.38	29.23	−54.38	−25.14	4.09
23E	44.55	28.84	−44.55	−15.72	13.12
24E	43.63	29.24	−43.63	−14.39	14.85
25E	46.40	30.58	−46.40	−15.81	14.77
26E	48.93	31.71	−48.93	−17.22	14.49
27E	50.55	34.92	−50.55	−15.63	19.29
28E	54.24	34.86	−54.24	−19.38	15.48
29E	53.08	31.61	−53.08	−21.48	10.13
30E	61.16	36.58	−61.16	−24.58	12.00
31E	51.93	30.96	−51.93	−20.97	9.99
32E	49.39	35.64	−49.39	−13.75	21.89
33E	49.86	35.28	−49.86	−14.58	20.70
34E	49.86	34.47	−49.86	−15.39	19.08
35E	50.32	34.81	−50.32	−15.51	19.30
36E	50.55	36.05	−50.55	−14.50	21.55
37E	50.55	36.25	−50.55	−14.30	21.95
38E	50.55	35.75	−50.55	−14.80	20.95
39E	50.55	34.30	−50.55	−16.24	18.06
40E	50.55	36.11	−50.55	−14.44	21.67
41E	50.78	35.26	−50.78	−15.52	19.74
42E	50.78	34.43	−50.78	−16.35	18.08
43E	57.70	38.64	−57.7	−19.05	19.59
44E	60.00	34.87	−60.00	−25.13	9.74
45E	47.32	32.97	−47.32	−14.35	18.62
46E	47.78	32.38	−47.78	−15.40	16.98
47E	49.16	34.02	−49.16	−15.14	18.88
48E	52.16	34.24	−52.16	−17.92	16.32
49E	49.16	32.26	−49.16	−16.91	15.35
50E	51.47	34.22	−51.47	−17.25	16.97
51E	58.85	32.38	−58.85	−26.47	5.91
52E	57.93	33.29	−57.93	−24.64	8.65
53E	56.77	30.05	−56.77	−26.73	3.32
54E	61.73	34.15	−61.73	−27.58	6.57
55E	69.23	37.58	−69.23	−31.65	5.93
56E	58.92	32.32	−58.92	−26.60	5.72
57E	60.53	33.49	−60.53	−27.04	6.45
58E	60.70	33.48	−60.70	−27.22	6.26
59E	60.90	33.67	−60.90	−27.23	6.44
60E	61.62	33.82	−61.62	−27.80	6.02
61E	63.46	35.36	−63.46	−28.10	7.26
62E	57.74	32.01	−57.74	−25.73	6.28
63E	61.52	33.97	−61.52	−27.56	6.41
64E	62.84	34.36	−62.84	−28.48	5.88
65E	62.58	35.28	−62.58	−27.30	7.98
66E	51.47	27.97	−51.47	−23.50	4.47
67E	53.64	28.01	−53.64	−25.63	2.38
68E	60.86	33.59	−60.86	−27.26	6.33
69E	57.23	34.40	−57.23	−22.84	11.56
70E	40.06	27.57	−40.06	−12.48	15.09
H	0.00	0.00	0.00	0.00	0.00

[a] $\Delta G^0(XE) = FE_{ox}(XE)$, $\Delta G^0(X) = -FE_{red}(X)$, the reference of $E_{ox}(XE)$ and $E_{red}(X)$ is $E(H^{+/0})$, and herein taking $E(H^{+/0}) = -1.902$ V vs SCE in acetonitrile. [b] $\Delta G^{\neq}(XE/X) = \Delta G^{\neq 0}(XE) + \Delta G^{\neq 0}(X)$, and the unit is kcal mol^{-1}.

and $\Delta G^{\neq 0}(\mathbf{28}) = -19.38$ kcal mol^{-1}, $\Delta G^{\neq 0}(\mathbf{28})$ and $\Delta G^{\neq 0}(\mathbf{1E})$ can be obtained using eq 7. The result is that $\Delta G^{\neq 0}(\mathbf{67})$ is −25.63 kcal mol^{-1} and $\Delta G^{\neq 0}(\mathbf{1E})$ is 30.44 kcal mol^{-1} in acetonitrile at 298 K. Using the same method, in this work, the thermo-kinetic parameter values of 70 organic compounds containing nitrogen, sulfur, and iron as electron donors (Scheme 1) and their conjugated cations as electron acceptors in acetonitrile at 298 K are reported (Table 1) because these organic compounds not only are commonly used as single-electron reducing agents or their conjugated cations as single-electron oxidizing agents in chemical research but also the second-order rate constants of their related electron transfer cross-reactions of XE with Y (Y ≠ X) in acetonitrile at 298 K can be obtained from the previous works in Nelsen's research group (see Table 2).[55,57−59] Herein, of course, the authors of this article should sincerely thank Stephen F. Nelsen and his co-workers for a lot of basic work of this paper.



33E **67** **33** **67E** (19)



1E **28** **1** **28E** (20)

Magnitude and Sign of Thermo-Kinetic Parameters of Electron Donors and Electron Acceptors

From the third column in Table 1, it is clear that the scale of thermo-kinetic parameter values of the 70 electron donors (**1E**−**70E**) in acetonitrile at 298 K ranges from 38.46 kcal mol^{-1} for **43E** to 24.52 kcal mol^{-1} for **8E**. According to the unit and sign of the thermo-kinetic parameter values of

Table 2. Redox Potentials of XE and Y as well as Second-Order Rate Constants of 70 Electron Transfer Reactions in Acetonitrile at 298 K, Which Are All Derived from Nelsen's Publications[55,57−59]

			XE + Y → X + YE					
no.	XE	Y	E_{ox}(XE)[a]	E_{red}(Y)[b]	ΔG^{0}[c]	k_2	$\Delta G^{\neq}$[d]	ref
1	**4E**	**6**	−0.109	0.058	−3.85	1.35×10^{6}	9.09	55
2	**6E**	**2**	0.058	0.281	−5.14	6.30×10^{6}	8.17	55
3	**3E**	**33**	0.124	0.260	−3.14	1.60×10^{3}	13.08	55
4	**5E**	**33**	0.010	0.260	−5.77	2.60×10^{2}	14.15	55
5	**6E**	**33**	0.058	0.260	−4.66	5.50×10^{1}	15.07	55
6	**8E**	**33**	−0.530	0.260	−18.22	3.20×10^{5}	9.94	55
7	**10E**	**33**	−0.241	0.260	−11.55	1.10×10^{4}	11.93	55
8	**9E**	**33**	−0.298	0.260	−12.87	3.10×10^{4}	11.32	55
9	**17E**	**33**	0.020	0.260	−5.53	4.90×10^{4}	11.05	55
10	**24E**	**33**	−0.010	0.260	−6.23	1.10×10^{2}	14.66	55
11	**26E**	**33**	0.220	0.260	−0.92	1.70×10^{0}	17.13	55
12	**33E**	**28**	0.260	0.450	−4.38	1.35×10^{1}	15.90	55
13	**33E**	**18**	0.260	0.290	−0.69	7.70×10^{2}	13.51	55
14	**3E**	**34**	0.124	0.260	−3.14	6.20×10^{3}	12.27	55
15	**3E**	**28**	0.124	0.450	−7.52	5.30×10^{6}	8.28	55
16	**1E**	**28**	0.395	0.450	−1.27	4.80×10^{4}	11.06	55
17	**33E**	**66**	0.260	0.330	−1.61	1.43×10^{4}	11.78	55
18	**13E**	**2**	0.110	0.281	−3.94	3.20×10^{5}	9.94	57
19	**11E**	**3**	0.080	0.124	−1.01	5.90×10^{4}	10.94	57
20	**12E**	**3**	−0.100	0.124	−5.17	8.10×10^{5}	9.39	57
21	**3E**	**14**	0.124	0.260	−3.14	1.31×10^{6}	9.10	57
22	**35E**	**18**	0.280	0.290	−0.23	1.70×10^{3}	13.04	57
23	**36E**	**18**	0.290	0.290	0.00	2.10×10^{2}	14.28	57
24	**37E**	**18**	0.290	0.290	0.00	1.49×10^{2}	14.48	57
25	**40E**	**18**	0.290	0.290	0.00	1.90×10^{2}	14.34	57
26	**70E**	**26**	−0.165	0.220	−8.88	1.60×10^{5}	10.35	57
27	**33E**	**67**	0.260	0.424	−3.78	5.20×10^{5}	9.65	57
28	**32E**	**67**	0.240	0.424	−4.24	2.80×10^{5}	10.02	57
29	**38E**	**67**	0.290	0.424	−3.09	2.35×10^{5}	10.12	57
30	**28E**	**51**	0.450	0.650	−4.61	4.40×10^{6}	8.39	58
31	**28E**	**52**	0.450	0.610	−3.69	1.98×10^{5}	10.22	58
32	**26E**	**15**	0.220	0.480	−6.00	3.40×10^{5}	9.90	58
33	**25E**	**2**	0.110	0.281	−3.94	1.30×10^{6}	9.11	58
34	**33E**	**29**	0.260	0.400	−3.23	4.70×10^{2}	13.80	58
35	**27E**	**15**	0.290	0.480	−4.38	1.50×10^{3}	13.11	58
36	**39E**	**66**	0.290	0.330	−0.92	7.40×10^{4}	10.81	58
37	**46E**	**18**	0.170	0.290	−2.77	1.02×10^{5}	10.62	58
38	**48E**	**67**	0.360	0.424	−1.48	3.00×10^{6}	8.61	58
39	**47E**	**18**	0.230	0.290	−1.38	6.40×10^{3}	12.26	58
40	**41E**	**67**	0.300	0.424	−2.86	5.40×10^{5}	9.63	58
41	**42E**	**66**	0.300	0.330	−0.69	6.00×10^{4}	10.93	58
42	**49E**	**15**	0.230	0.480	−5.77	1.35×10^{5}	10.45	58
43	**50E**	**15**	0.330	0.480	−3.46	4.90×10^{3}	12.41	58
44	**7E**	**15**	0.150	0.480	−7.61	9.40×10^{4}	10.66	59
45	**43E**	**68**	0.600	0.737	−3.16	2.80×10^{4}	11.38	59
46	**23E**	**14**	0.030	0.260	−5.30	1.80×10^{5}	10.28	59
47	**16E**	**18**	0.185	0.290	−2.42	5.20×10^{6}	8.29	59
48	**19E**	**28**	0.350	0.450	−2.31	1.19×10^{6}	9.16	59
49	**28E**	**20**	0.450	0.490	−0.92	3.10×10^{5}	9.96	59
50	**34E**	**21**	0.260	0.510	−5.77	1.86×10^{5}	10.26	59
51	**69E**	**52**	0.580	0.610	−0.69	4.30×10^{5}	9.76	59
52	**34E**	**53**	0.260	0.560	−6.92	1.30×10^{7}	7.74	59
53	**33E**	**30**	0.260	0.750	−11.30	8.80×10^{4}	10.70	59
54	**43E**	**30**	0.600	0.750	−3.46	3.00×10^{2}	14.07	59
55	**45E**	**28**	0.150	0.450	−6.92	6.70×10^{2}	13.59	59
56	**31E**	**28**	0.350	0.450	−2.31	2.00×10^{4}	11.58	59
57	**43E**	**55**	0.600	1.100	−11.53	4.60×10^{7}	7.00	59
58	**33E**	**22**	0.260	0.456	−4.52	2.30×10^{5}	10.13	59

Table 2. continued

no.	XE	Y	XE + Y → X + YE					ref
			E_{ox}(XE)[a]	E_{red}(Y)[b]	ΔG^{0}[c]	k_2	$\Delta G^{\neq}$[d]	
59	**33E**	**54**	0.260	0.775	−11.88	1.40×10^{7}	7.70	59
60	**44E**	**54**	0.700	0.775	−1.73	2.80×10^{7}	7.29	59
61	**43E**	**61**	0.600	0.850	−5.77	1.15×10^{5}	10.54	59
62	**43E**	**58**	0.600	0.730	−3.00	2.60×10^{4}	11.42	59
63	**43E**	**60**	0.600	0.770	−3.92	6.90×10^{4}	10.85	59
64	**43E**	**64**	0.600	0.823	−5.14	2.20×10^{5}	10.16	59
65	**43E**	**63**	0.600	0.766	−3.83	4.60×10^{4}	11.09	59
66	**43E**	**65**	0.600	0.812	−4.89	3.00×10^{4}	11.34	59
67	**37E**	**59**	0.290	0.739	−10.35	1.50×10^{6}	9.02	59
68	**37E**	**56**	0.290	0.653	−8.37	5.20×10^{5}	9.65	59
69	**37E**	**57**	0.290	0.723	−9.98	1.10×10^{6}	9.21	59
70	**43E**	**62**	0.600	0.602	−0.05	2.10×10^{3}	12.92	59

[a] E_{ox}(XE) is the oxidation potential of XE, and the unit is V vs SCE in acetonitrile. [b] E_{red}(Y) is reduction potential of Y, and the unit is V vs SCE in acetonitrile. [c] $\Delta G^{0} = -23.06 \times [E_{red}(Y) - E_{ox}(XE)]$ (kcal mol^{-1}). [d] $\Delta G^{\neq} = -0.592 \times (\ln k_2 - 29.45)$ (kcal mol^{-1}).

electron donors, the thermo-kinetic parameter of the electron donor $\Delta G^{\neq 0}$(XE) has at least three characterizations: (i) The nature of the thermo-kinetic parameter of electron donors is a type of energy of electron donors because the unit of the parameter is kcal mol^{-1}. (ii) The thermo-kinetic parameter values of electron donors are always positive, which means that electron donors in electron transfer reactions require free energy to release electrons. (iii) The more positive the thermo-kinetic parameter value of electron donors, the smaller the electron-releasing activity of the electron donors. The reason is that the more positive the thermo-kinetic parameter value of electron donors, the larger the activation free energy of the electron transfer reactions. Among the 70 electron donors in Scheme 1, the electron-releasing activity of **43E** is the smallest, but the electron-releasing activity of **8E** is the greatest.

The fifth column in Table 1 shows that the scale of the thermo-kinetic parameter values of the 70 electron acceptors (X) in acetonitrile at 298 K ranges from −7.12 kcal mol^{-1} for **8** to −31.65 kcal mol^{-1} for **55**. According to the unit and sign of the thermo-kinetic parameter value of the electron acceptor, the thermo-kinetic parameter of the electron acceptor $\Delta G^{\neq 0}$(X) also has three characterizations: (i) The nature of the thermo-kinetic parameter of electron acceptors is a type of energy of electron acceptors because the unit of the parameter is kcal mol^{-1}. (ii) Thermo-kinetic parameter values of electron acceptors are all negative, which means that electron acceptors in electron transfer reactions always release free energy to get electrons. (iii) The more negative the thermo-kinetic parameter value of electron acceptors, the larger the electron-accepting activity of the electron acceptors because the more negative the thermo-kinetic parameter value of electron acceptors, the smaller the activation free energy of the reactions. Evidently, among the 70 electron acceptors in Table 1, the electron-accepting activity of **8** is the smallest, but the electron-accepting activity of **55** is the greatest.

Predictions of the Activation Free Energies of 4900 Electron Transfer Reactions

Since the thermo-kinetic parameter values of the 70 electron donors (**1E**−**70E**) and the thermo-kinetic parameter values of the 70 electron acceptors (**1**−**70**) in acetonitrile at 298 K have been determined, the activation free energies and the corresponding second-order rate constants of 4900 electron transfer reactions in acetonitrile at 298 K can be estimated according to the thermo-kinetic parameter values of the 70 electron acceptors and the 70 electron acceptors using eq 7 and Eyring equation. The detailed results are provided in Table S1. From Table S1, it is clear that the activation free energies (or the corresponding second-order rate constants) of the 4900 electron transfer reactions in acetonitrile at 298 K range from 31.34 kcal mol^{-1} (or 6.59×10^{-11} M^{-1} s^{-1}) for the reaction of **43E** with **8** to −7.13 kcal mol^{-1} (or 1.04×10^{18} M^{-1} s^{-1}) for the reaction of **8E** with **55**. In general, if the activation free energy (or the second-order rate constant) of a chemical reaction is larger than 25.64 kcal mol^{-1} (or smaller than 1×10^{-6} M^{-1} s^{-1}), the chemical reaction is considered not to proceed. If the activation free energy (or the second-order rate constant) of a chemical reaction is less than 3.81 kcal mol^{-1} (or larger than 1×10^{10} M^{-1} s^{-1}), the chemical reaction is considered to be diffusion controlled. If the activation free energy (or the second-order rate constant) of a chemical reaction is smaller than 25.64 kcal mol^{-1} (or larger than 1×10^{-6} M^{-1} s^{-1}) but larger than 20.18 kcal mol^{-1} (or smaller than 1×10^{-2} M^{-1} s^{-1}), the chemical reaction is called as a slow chemical reaction. If the activation free energy (or the second-order rate constant) of a chemical reaction is smaller than 20.18 kcal mol^{-1} (or larger than 1×10^{-2} M^{-1} s^{-1}) but larger than 13.36 kcal mol^{-1} (or smaller than 1×10^{3} M^{-1} s^{-1}), the chemical reaction is called as a general-rate reaction. If the activation free energy (or the second-order rate constant) of a chemical reaction is smaller than 13.36 kcal mol^{-1} (or larger than 1×10^{3} M^{-1} s^{-1}) but larger than 9.26 kcal mol^{-1} (or smaller than 1×10^{6} M^{-1} s^{-1}), the chemical reaction is called as a fast reaction. If the activation free energy (or the second-order rate constant) of a chemical reaction is smaller than 9.26 kcal mol^{-1} (or larger than 1×10^{6} M^{-1} s^{-1}) but larger than 3.81 kcal mol^{-1} (or smaller than 1×10^{10} M^{-1} s^{-1}), the chemical reaction is called as an ultrafast chemical reaction. If the activation free energy of a chemical reaction is negative, a charge-transfer complex (CT complex) as a reaction intermediate is formed in the course of the electron transfer process because the formation free energy of the CT complex can make the activation free energy of the ET reaction become negative. In fact, it has been extensively reported that chemical reactions, especially fast ET reactions, have negative activation free energy.[60−91] Since the activation free energy of ET reaction controlled by diffusion in acetonitrile is 3.81 kcal/mol, if the activation free energy in Table S1 is smaller than 3.81 kcal mol^{-1}, the CT complex as a reaction intermediate can be

Table 3. Comparison of the Predicted Values with the Experimental Values on the Activation Free Energies (kcal mol^{-1}) of 65 Electron Transfer Reactions in Acetonitrile at 298 K

no.	XE/Y	$\Delta G^{\neq 0}$(XE)	$\Delta G^{\neq 0}$(Y)	$\Delta G^{\neq}$(pred)	$\Delta G^{\neq}$(exp)	ref	$\Delta\Delta G^{\neq}$
1	**1E**/**15**	30.44	−21.81	8.63	8.52	58	0.11
2	**5E**/**26**	28.73	−17.22	11.51	11.27	55	0.24
3	**5E**/**28**	28.73	−19.38	9.35	9.37	55	−0.02
4	**6E**/**14**	29.65	−18.56	11.09	11.09	57	0.01
5	**6E**/**28**	29.65	−19.38	10.27	10.16	55	0.11
6	**6E**/**34**	29.65	−15.39	14.26	14.18	55	0.09
7	**7E**/**18**	32.47	−21.77	10.70	10.39	59	0.31
8	**7E**/**29**	32.47	−21.48	10.99	10.95	59	0.04
9	**9E**/**34**	25.9	−15.39	10.51	10.51	55	0.00
10	**10E**/**12**	26.51	−13.11	13.41	13.28	57	0.13
11	**10E**/**34**	26.51	−15.39	11.13	11.23	55	−0.10
12	**12E**/**4**	28.45	−16.71	11.73	11.79	57	−0.06
13	**18E**/**28**	28.78	−19.38	9.40	9.28	57	0.13
14	**23E**/**26**	28.84	−17.22	11.61	11.30	59	0.31
15	**24E**/**14**	29.24	−18.56	10.68	10.62	57	0.07
16	**24E**/**34**	29.24	−15.39	13.85	13.50	55	0.35
17	**25E**/**18**	30.58	−21.77	8.82	8.52	58	0.29
18	**26E**/**18**	31.71	−21.77	9.94	9.75	55	0.19
19	**26E**/**28**	31.71	−19.38	12.33	12.56	55	−0.23
20	**26E**/**29**	31.71	−21.48	10.23	10.16	58	0.07
21	**26E**/**34**	31.71	−15.39	16.32	16.44	55	−0.11
22	**27E**/**1**	34.92	−22.53	12.39	12.61	58	−0.22
23	**28E**/**15**	34.86	−21.81	13.05	12.74	58	0.31
24	**29E**/**15**	31.61	−21.81	9.80	9.76	58	0.04
25	**29E**/**28**	31.61	−19.38	12.23	12.10	58	0.13
26	**31E**/**15**	30.96	−21.81	9.15	9.02	59	0.13
27	**33E**/**15**	35.28	−21.81	13.47	13.34	58	0.13
28	**33E**/**19**	35.28	−23.39	11.89	12.12	59	−0.23
29	**33E**/**20**	35.28	−24.9	10.38	10.57	59	−0.19
30	**33E**/**21**	35.28	−24.21	11.07	11.10	59	−0.03
31	**33E**/**34**	35.28	−15.39	19.89	20.08	55	−0.19
32	**33E**/**51**	35.28	−26.47	8.81	8.98	58	-0.18
33	**33E**/**56**	35.28	−26.6	8.68	8.77	59	−0.09
34	**34E**/**15**	34.47	−21.81	12.66	12.84	58	−0.17
35	**34E**/**19**	34.47	−23.39	11.08	11.07	59	0.00
36	**34E**/**20**	34.47	−24.9	9.57	9.43	59	0.13
37	**34E**/**22**	34.47	−25.14	9.33	9.37	59	−0.05
38	**34E**/**28**	34.47	−19.38	15.09	15.29	55	−0.20
39	**34E**/**29**	34.47	−21.48	12.99	13.33	58	−0.34
40	**34E**/**51**	34.47	−26.47	8.00	8.37	59	−0.37
41	**34E**/**52**	34.47	−24.64	9.83	9.56	58	0.28
42	**36E**/**66**	36.05	−23.5	12.55	12.46	57	0.08
43	**36E**/**67**	36.05	−25.63	10.42	10.60	57	−0.18
44	**37E**/**54**	36.25	−27.58	8.67	8.81	59	−0.14
45	**37E**/**60**	36.25	−27.8	8.45	8.49	59	−0.03
46	**37E**/**61**	36.25	−28.1	8.15	8.40	59	−0.25
47	**37E**/**63**	36.25	−27.56	8.69	8.70	59	−0.01
48	**37E**/**66**	36.25	−23.5	12.75	12.43	57	0.33
49	**37E**/**67**	36.25	−25.63	10.62	10.58	57	0.04
50	**38E**/**18**	35.75	−21.77	13.98	13.73	57	0.25
51	**38E**/**66**	35.75	−23.5	12.25	11.87	57	0.38
52	**40E**/**54**	36.11	−27.58	8.53	8.41	59	0.12
53	**40E**/**60**	36.11	−27.8	8.31	7.95	59	0.36
54	**40E**/**66**	36.11	−23.5	12.61	12.30	57	0.31
55	**41E**/**18**	35.26	−21.77	13.49	13.76	59	−0.28
56	**43E**/**54**	38.64	−27.58	11.07	11.11	59	−0.05
57	**43E**/**56**	38.64	−26.6	12.04	12.30	59	−0.26
58	**43E**/**57**	38.64	−27.04	11.60	11.68	59	−0.08
59	**43E**/**59**	38.64	−27.23	11.42	11.32	59	0.09
60	**49E**/**18**	32.26	−21.77	10.49	10.39	59	0.10

Table 3. continued

no.	XE/Y	$\Delta G^{\neq 0}$(XE)	$\Delta G^{\neq 0}$(Y)	$\Delta G^{\neq}$(pred)	$\Delta G^{\neq}$(exp)	ref	$\Delta\Delta G^{\neq}$
61	**49E**/29	32.26	−21.48	10.78	10.43	59	0.35
62	**50E**/21	34.22	−24.21	10.01	10.16	59	−0.15
63	**66E**/28	27.97	−19.38	8.59	8.26	57	0.33
66	**67E**/28	28.01	−19.38	8.63	8.77	59	−0.14
65	**70E**/4	27.57	−16.71	10.86	11.17	57	−0.31

formed in the course of the electron transfer process. From these criteria, we can know the type to which each electron transfer reaction listed in Table S1 belongs. In laboratories, for the slow and general-rate chemical reactions, the second-order rate constants can be determined using the conventional UV−vis spectroscopy technique; for the fast chemical reactions, the second-order rate constant can be determined using the stopped-flow technique; but for ultrafast chemical reactions, the second-order rate constant is only indirectly determined using the laser flashing photolysis technique. Because the electron transfer reactions listed in Table S1 are generally the common and important electron transfer reactions and extensively applied in chemical industries and chemical laboratories, obviously, the data in Table S1 should be very useful for the synthetic chemists, material chemists, energy chemists, etc., who are engaged in research and use of these electron transfer reactions.

Reliability of eq 7 to Predict the Activation Free Energies of Electron Transfer Reactions

In this work, we have predicted the activation free energies and second-order rate constants of 4900 electron transfer reactions based on the thermo-kinetic parameters of 70 electron donors and 70 acceptors using eq 7 (Table S1). To verify the predicted values shown in Table S1, the activation free energy values of 65 electron transfer reactions in Table S1 can be examined because their second-order rate constants can be measured. Table 3 summarizes the predicted $\Delta G^{\neq}$ values of 65 electron transfer reactions using eq 7 and the corresponding independent experimental results in acetonitrile at 298 K. By comparing the measured $\Delta G^{\neq}$(exp) values with the predicted $\Delta G^{\neq}$(pred) values using eq 7, it is found that the difference between the measured values and the corresponding predicted values for the 65 electron transfer reactions is smaller than 0.38 kcal mol^{-1}. The deviation of 0.38 kcal mol^{-1} is acceptable to the prediction of the activation free energies of electron transfer reactions according to the thermo-kinetic parameters of electron donors and electron acceptors because the span of the activation free energy change for the 65 reactions is as high as 12.13 kcal mol^{-1}, and the deviation of 0.38 kcal mol^{-1} is less than 4% relative to the span of activation free energy change (12.13 kcal mol^{-1}) of the 65 electron transfer reactions. In addition, when the measured values are plotted against the corresponding predicted values (Figure 1), it is found that the correlation coefficient (r) is 0.99137 and the slope is 1.00517. In general, if the correlation coefficient of the predicted values with the measured values is greater than two nines (0.99) and the slope is close to 1, the predicted values can be considered to agree well with the corresponding measured values. Clearly, Figure 1 indicates that eq 7 is reliable also to predict the activation free energies of electron transfer reactions.

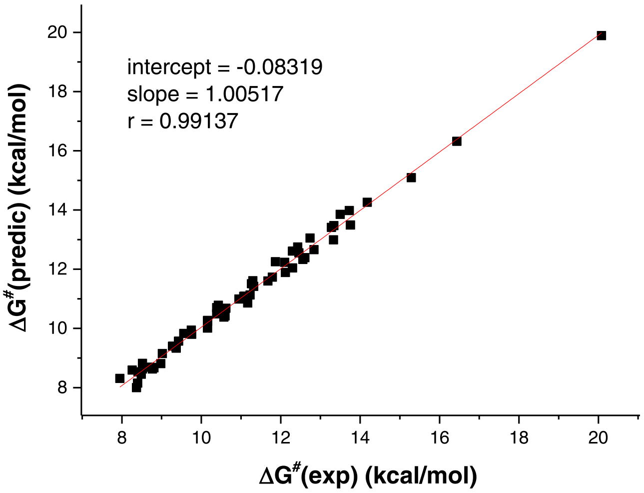
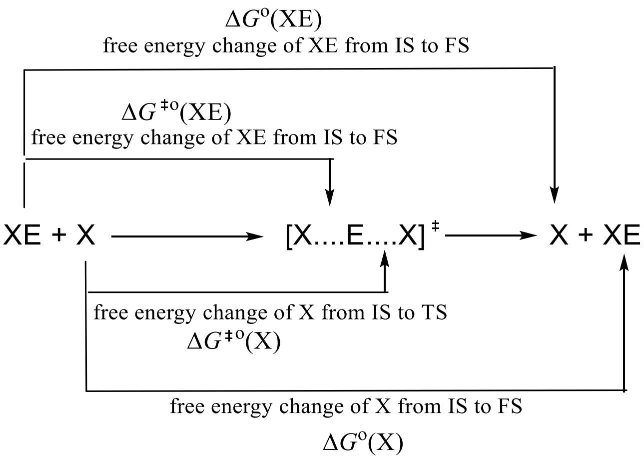


Figure 1. Plot of the experimental values with the corresponding predicted values for the activation free energies of 65 electron transfer reactions.

Physical Meaning of the Thermo-Kinetic Parameters of Electron Donors and Electron Acceptors

Since the thermo-kinetic parameter of electron donors and electron acceptors is a new characteristic energetic parameters of electron donors and electron acceptors and are all composed of one thermodynamic parameter and one kinetic parameter, the physical meaning of the thermo-kinetic parameter needs clarifying. For an electron self-exchange reaction (XE + X→ X + XE), eq 21 can be obtained from eq 7. In eq 21, $\Delta G^{\neq}$(XE/X) is the activation free energy of the electron self-exchange reaction (XE + X→ X + XE). Since $\Delta G^{\neq}$(XE/X) is consisted of $\Delta G^{\neq 0}$(XE) and $\Delta G^{\neq 0}$(X), the physical meaning of $\Delta G^{\neq 0}$(XE) and $\Delta G^{\neq 0}$(X) can be showed in Scheme 2. From

Scheme 2. Physical Meaning of $\Delta G^{\neq 0}$(XE) and $\Delta G^{\neq 0}$(X) as well as ΔG^{0}(XE) and ΔG^{0}(X)



Scheme 2, it is clear that the physical meaning of $\Delta G^{\neq 0}(\mathrm{XE})$ is the free energy change of XE going from the initial state to the transition state in the electron self-exchange reaction and the physical meaning of $\Delta G^{\neq 0}(\mathrm{X})$ is the free energy change of X from the initial state to the transition state in the electron self-exchange reaction. Since the transition of XE from the initial state to the transition state is a process of increasing free energy of XE, but the transition of X from the initial state to the transition state is a process of decreasing free energy of X, so the value of $\Delta G^{\neq 0}(\mathrm{XE})$ is always positive, but the value of $\Delta G^{\neq 0}(\mathrm{X})$ is always negative.

$$\Delta G^{\neq}(\mathrm{XE/X}) = \Delta G^{\neq 0}(\mathrm{XE}) + \Delta G^{\neq 0}(\mathrm{X}) \qquad (21)$$

Intrinsic Barrier of the Electron Donor to Donate Electrons and the Electron Acceptor to Accept Electrons

As is well-known, in an electron transfer reaction, the actual electron-donating ability of the electron donor (XE) and the actual electron-gaining ability of the electron acceptor (X) are dependent not only on the thermodynamic driving force of the electron donor (XE) to donate electrons and the thermodynamic driving force of the electron acceptor (X) to gain electrons but also on the intrinsic barrier of the electron donor to donate electrons and the intrinsic barrier of the electron acceptor to accept electrons. The thermodynamic driving force of the electron donor (XE) to donate electrons and the electron acceptor (X) to gain electrons can be quantitatively described by the oxidation potential of the electron donor and the reduction potential of the electron acceptor, respectively. However, the intrinsic barrier of the electron donor to donate electrons and the intrinsic barrier of the electron acceptor to accept electrons cannot be quantitatively described by a characteristic parameter of the electron donor and electron acceptor till now. To find a characteristic parameter of the electron donor and electron acceptor to quantitatively measure the intrinsic barrier of the electron donor to donate electrons and the electron acceptor to accept electrons, the activation free energy of the electron self-exchange reaction (XE + X → X + XE) is examined. For an electron self-exchange reaction (XE + X → X + XE), since the electron acceptor (X) and the electron donor (XE) have a conjugated relation with each other, the activation free energy of electron self-exchange reactions is a characteristic parameter of electron donors and electron acceptors. In addition, because the thermodynamic driving force of electron self-exchange reactions is zero, the activation free energy of electron self-exchange reactions is just the intrinsic barrier of the electron donor to donate electrons and the electron acceptor to gain electrons in electron transfer reactions. In other words, the intrinsic barrier of the electron donor to donate electrons and the electron acceptor to accept electrons can be quantitatively described by the activation free energy of electron self-exchange reactions. The larger the activation energy of the reactant electron self-exchange reaction, the larger the intrinsic barrier of electron donors and electron acceptors.

From the last column in Table 1, it is clear that the intrinsic barrier of the 70 electron donors (**1E**−**70E**) or the 70 electron donors (**1**−**70**) in acetonitrile at 298 K ranges from 2.38 kcal mol^{-1} for **67E** to 21.95 kcal mol^{-1} for **37E**. Among the 70 electron donors in Scheme 1, the intrinsic barrier of **67E** is the smallest, but the intrinsic barrier of **37E** is the greatest. Due to the small intrinsic barrier (2.38 kcal mol^{-1}), **67E** and its analogues should be the best organic electrode material. In fact, many chemists engaged in battery chemistry and application research are developing **67E** and its analogues as a new material for battery electrodes. When the relationship of the intrinsic barrier of the electron donor with its structure is examined, it is found that (1) the intrinsic barrier of an electron donor with a planar structure is generally much smaller than that of an electron donor with a three-dimensional structure. (2) The intrinsic barrier of aromatic electron donors is generally much smaller than that of nonaromatic electron donors. The main reason may be that the electron donors and electron acceptors with planar or aromatic structures in the reaction transition state are conducive to the accumulation of reactants. Since the activation free energy of electron self-exchange reactions is merely a characteristic energetic parameter of electron donors and electron acceptors to quantitatively describe their intrinsic barriers in electron transfer reactions, the activation free energy of electron self-exchange reactions should be a very important parameter of electron donors and electron acceptors and has a wide range of applications.

Relationship of $\Delta G^{\neq 0}$(XE) with ΔG^{0}(XE) for Electron Donors

$\Delta G^{0}(\mathrm{XE})$ is a thermodynamic parameter of electron donors, and the value can quantitatively describe the electron-donating ability of electron donors. $\Delta G^{\neq 0}(\mathrm{XE})$ is a kinetic parameter of electron donors, and the value can quantitatively describe the electron-donating activity of electron donors. What is the relationship between them? According to the definition equation of $\Delta G^{\neq 0}(\mathrm{XE})$ (eq 10), it is clear that $\Delta G^{\neq 0}(\mathrm{XE})$ is jointly determined by the two terms $\Delta G^{\neq}(\mathrm{XE/X})$ and $\Delta G^{0}(\mathrm{XE})$, and $\Delta G^{\neq}(\mathrm{XE/X})$ can change with XE change, which means that the increase of $\Delta G^{0}(\mathrm{XE})$ does not necessarily mean the increase of $\Delta G^{\neq 0}(\mathrm{XE})$. For example, ΔG^{0}(**67E**) (53.64 kcal mol^{-1}) is greater than ΔG^{0}(**13E**) (46.40 kcal mol^{-1}) but $\Delta G^{\neq 0}$(**67E**) (28.01 kcal mol^{-1}) is smaller than $\Delta G^{\neq 0}$(**13E**) (31.42 kcal mol^{-1}) (Table 1), the reason is that $\Delta G^{\neq}$(**67E**/**67**) (2.36 kcal mol^{-1}) is much smaller than $\Delta G^{\neq}$(**13E**/**13**) (16.44 kcal mol^{-1}), which makes $\Delta G^{\neq 0}$(**67E**) (28.01 kcal mol^{-1}) become smaller than $\Delta G^{\neq 0}$(**13E**) (31.42 kcal mol^{-1}). Figure 2 shows the depend-

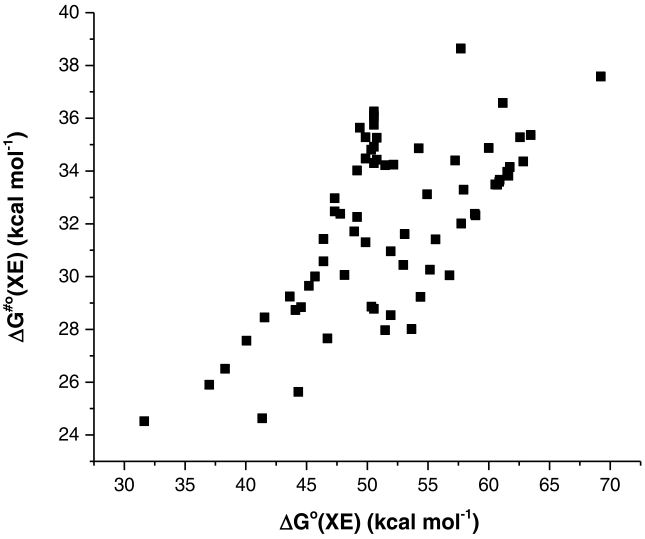


Figure 2. Relationship of thermo-kinetic parameters of electron donors (XE) with the molar free energy change of XE to release electrons in acetonitrile at 298 K.

ence of $\Delta G^{\neq 0}$(XE) on ΔG^0(XE) for the 70 XE in Table 1. From Figure 2, it is clear that the 70 points in the figure are relatively scattered, which means that there is no linear relationship between $\Delta G^{\neq 0}$(XE) and ΔG^0(XE) for the 70 electron donors. Although $\Delta G^{\neq 0}$(XE) has no linear relationship with ΔG^0(XE) for electron donors, the general trend of $\Delta G^{\neq 0}$(XE) change with ΔG^0(XE) change for the 70 electron donors is that $\Delta G^{\neq 0}$(XE) increases with the increase of ΔG^0(XE), which means that for the 70 electron donors, the contribution of ΔG^0(XE) to $\Delta G^{\neq 0}$(XE) is much greater than the contribution of $\Delta G^{\neq}$(XE/X) to $\Delta G^{\neq 0}$(XE).

Relationship of $\Delta G^{\neq 0}$(X) with ΔG^0(X) for Electron Acceptors

The relationship of $\Delta G^{\neq 0}$(X) with ΔG^0(X) for electron acceptors is somewhat similar to the relationship of $\Delta G^{\neq 0}$(XE) with ΔG^0(XE) for electron donors. But there are two major differences between them: (1) The dispersion degree of the relationship points of $\Delta G^{\neq 0}$(X) with ΔG^0(X) for the 70 electron acceptors (Figure 3) is much smaller than the dispersion degree of the relationship points of $\Delta G^{\neq 0}$(XE) with ΔG^0(XE) for the 70 electron donors (Figure 2). (2) In absolute value, the difference between $\Delta G^{\neq 0}$(X) and ΔG^0(X) is always greater than the difference between $\Delta G^{\neq 0}$(XE) and ΔG^0(XE), that is, $\Delta G^{\neq 0}$(X) in absolute value is always less than ΔG^0(XE). The main reason for the two differences is that from the initial state to the transition state, the free energy change of the electron donors is always greater than the free energy change of the corresponding electron acceptors.

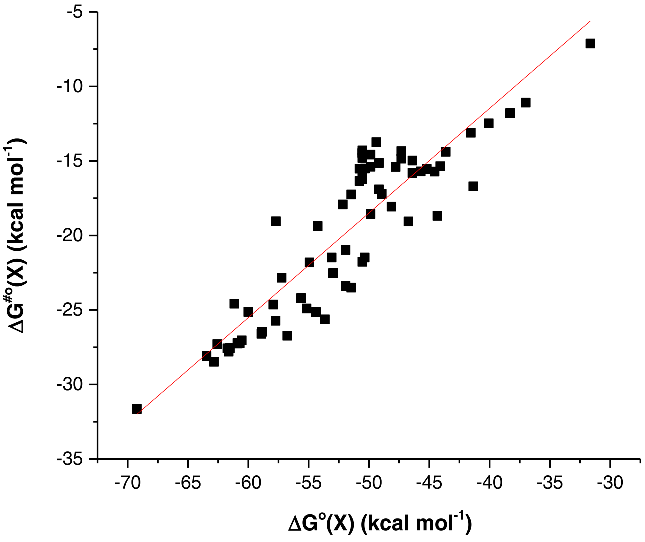


Figure 3. Relationship of thermo-kinetic parameters of electron acceptors (X) with the molar free energy change of X to accept electrons in acetonitrile at 298 K.

Relationship of Activation Free Energy ($\Delta G^{\neq}$) with the Thermodynamic Driving Force (ΔG^0) for Electron Transfer Reactions

It is well-known that the relationship between the activation free energy and the thermodynamic driving force for electron transfer reactions has been a subject of debate. Marcus[26,27] believed that the relationship of activation free energy with the thermodynamic driving force for electron transfer reactions is of parabolic line; that is, the dependence of the activation free energy on the thermodynamic driving force can be divided into two stages: (1) When the thermodynamic driving force of electron transfer reactions is less than a constant (λ, reorganization energy of electron transfer reactions), the activation free energy of electron transfer reactions decreases with the increase of the thermodynamic driving force; (2) When the thermodynamic driving force of electron transfer reactions is greater than a constant (λ, reorganization energy of electron transfer reactions), the activation free energy of the electron transfer reaction increases as the thermodynamic driving force of the reaction becomes larger (i.e., inverted region). However, Rehm−Weller's view on the relationship of activation free energy with the thermodynamic driving force for electron transfer reactions[29] is different from Marcus' view. They believe that the relationship of activation free energy with the thermodynamic driving force for electron transfer reactions is a linear relationship rather than a parabolic relationship. In fact, both views are incorrect.[92−94] To elucidate the real relationships of activation free energy with the thermodynamic driving force for electron transfer reactions, the dependence of activation free energy on the corresponding thermodynamic driving force for the 70 electron transfer reactions listed in Table 2 is examined (see Figure 4).

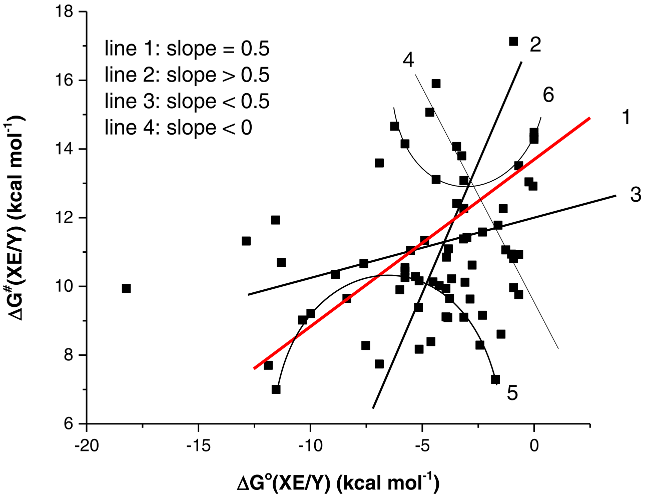


Figure 4. Relationship between activation free energy $\Delta G^{\neq}$(XE/Y) and thermodynamic driving force ΔG^0(XE/Y) for the 70 electron transfer reactions in acetonitrile at 298 K listed in Table 2.

From Figure 4, it is clear that the distribution of these 70 relationship points is neither linear nor parabolic but is sporadic. Of course, if some special relationship points among the 70 relationship points would be chosen intentionally to examine the dependence of $\Delta G^{\neq}$ on ΔG^0, various linear and nonlinear observed relationships between $\Delta G^{\neq}$ and ΔG^0 can be found, which indicates that the relationship between $\Delta G^{\neq}$ and ΔG^0 is uncertainty. The reason is that $\Delta G^{\neq}$ of a chemical reaction is not only determined by the thermodynamic driving force of the chemical reactions but also determined by the resistant force (i.e., intrinsic barrier), and the intrinsic barrier is also changed with the change of reactants. According to eq 5, it is clear that if the intrinsic barriers of the reactions are the same or close to each other, that is, if the intrinsic barriers of the reactions remain the same, the change of $\Delta G^{\neq}$ with the change of ΔG^0 is linear, and the slope of the straight line is 0.5. The points on Line 1 in Figure 4 have linear relationship between their $\Delta G^{\neq}$ and ΔG^0 and the slope of the line is 0.5, so the

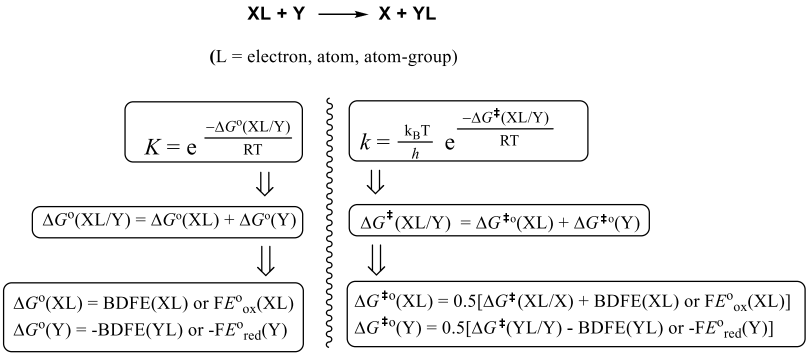


Figure 5. Symmetry and unification of kinetic equations with the corresponding thermodynamic equations for chemical reactions.

intrinsic barrier of the reactions are the same or close to each other. It should be noted here that if the slope of the straight line (such as the lines 2, 3, and 4) is not equal to 0.5, the intrinsic barrier of the reactions on the same line are not the same. In other words, the intrinsic barrier of reactions is change as the change of the reactants. In detail, if the slope is smaller than 0.5 (such as lines 3 and 4 in Figure 4), the intrinsic barrier of the reactions will increase linearly with the increase of the corresponding ΔG^0. If the slope is larger than 0.5 (such as line 2 in Figure 4), the intrinsic barrier of the reactions will decrease linearly with the increase of the corresponding ΔG^0. If the dependence line of $\Delta G^{\neq}$ on the corresponding ΔG^0 for some reactions is parabolic (such as lines 5 and 6 in Figure 4), the increase or decrease of the intrinsic barrier for the reactions with the increase of the corresponding ΔG^0 is nonlinear.

Symmetrical Unification Between Thermodynamic Equations and the Corresponding Kinetic Equations

Chemical thermodynamics and chemical kinetics are two different disciplines to study chemical reactions. Chemical thermodynamics is mainly to study the equilibrium constant of a chemical reaction, i.e., to study the energetic difference between the initial state and the final state of a chemical reaction. The main purpose is to establish the quantitative relationship between the equilibrium constant and free energy change of a chemical reaction, as well as the quantitative relationship between the free energy change of a chemical reaction and the characteristic parameters of each reactant. Chemical kinetics is mainly to study the rate constants of a chemical reaction, i.e., to study the difference of free energy between the initial state and the transition state of a chemical reaction. The main purpose is to establish the quantitative relationship between the rate constants and the activation free energy, as well as the quantitative relationship between the activation free energy and characteristic parameters of each reactant.

For the thermodynamics of a chemical reaction, as the thermodynamic theory has matured after more than 100 years of development, the quantitative relationship between the equilibrium constants and the thermodynamic driving force (i.e., free energy change) of a chemical reaction as well as the quantitative relationship between the free energy change of a chemical reaction and the thermodynamic characteristic parameters of the reactants have been established. The equilibrium constant (K) and the thermodynamic driving force (ΔG^0) of a chemical reaction can be directly calculated using the corresponding thermodynamic characteristic parameters of the reactants, such as bond dissociation free energy (BDFE), redox potential ($E_{1/2}$) according to the related thermodynamic equations shown in Figure 5. However, for kinetics of a chemical reaction, due to much more factors affecting the rate constant than that affecting the equilibrium constant, the development of chemical kinetic theory has not matured till now. Although the quantitative relationship between the rate constant and the activation free energy of a chemical reactant has been established, no quantitative relationship between the activation free energy and the kinetic characteristic parameters of reactants can be found. The main reason is that no kinetic characteristic parameters of reactants can be used to quantitatively describe the activity of the reactant. In this work and our previous work,[41−51] we have proposed a characteristic activity parameter of reactants named as the thermo-kinetic parameter of reactants according to the thermodynamic characteristic parameter of reactants and the activation free energy of the corresponding self-reaction of the reactants to quantitatively describe the activity of the reactant. Since the thermo-kinetic parameter of reactants enables the activation free energy of reactions like the equilibrium constant of reactions to be calculated based on only one characteristic parameter of the reactants, the thermo-kinetic parameter of reactants makes the kinetic equations of a chemical reaction and the corresponding thermodynamic equations show symmetry and unification (Figure 5).

■ CONCLUSIONS

In this work, the definition formulae of the thermo-kinetic parameters of reductants and oxidants were made according to the redox potentials of the reductants and oxidants and the activation free energy of the corresponding self-reactions of reactants. The thermo-kinetic parameter values of 70 well-known electron donors and the corresponding 70 conjugated electron acceptors in acetonitrile at 298 K are determined according to the reported Nelsen's work. The activation free energies of 4900 typical electron transfer reactions in acetonitrile are estimated according to the thermo-kinetic parameter values of 70 electron donors and 70 conjugated electron acceptors. After the reliabilities of the predicted results, the physical meaning of the thermo-kinetic parameter of reductants and oxidants, and the relationships of the thermo-kinetic parameter of reductants and oxidants with their redox potentials as well as the relationships of the activation free energy of the 70 electron transfer reactions with their thermodynamic driving forces were examined, the following conclusions can be made.

(1) The thermo-kinetic parameters of electron donors and electron acceptors can be used to quantitatively describe

the electron-donating activity of electron donors and the electron-accepting activity of electron acceptors in the electron transfer reaction.

(2) The thermo-kinetic parameter of electron donors is always positive. The more positive the thermo-kinetic parameter value, the lower the electron-donating activity of the electron donor. The physical meaning of the thermo-kinetic parameter of electron donors is the free energy change of electron donors going from the initial state to the transition state in the electron self-exchange reaction, i.e., the free energy that the electron donor absorbs when the reaction proceeds from the initial state to the transition state.

(3) The thermo-kinetic parameter of electron acceptors is always negative. The more negative the value of the thermo-kinetic parameter, the higher the activity of the electron acceptor. The physical meaning of the thermo-kinetic parameter of the electron acceptor is the free energy change of the electron acceptor going from the initial state to the transition state in the electron self-exchange reaction, i.e., the free energy that the electron acceptor releases when the reaction proceeds from the initial state to the transition state.

(4) The thermo-kinetic parameter value of the electron donor is always greater than half of the electron dissociation energy. There is no linear free energy change relationship between the thermo-kinetic parameter of electron donors and their electron dissociation energies. However, if the activation energy of the electron self-exchange reaction remains the same or changes very little when the electron donor is changed, the change between the thermo-kinetic parameters of the electron donors and their electron dissociation energy has a linear free energy relationship.

(5) The relationship of the thermo-kinetic parameters of electron donors with their electron affinities is similar to that of the thermo-kinetic parameters of electron donors with their electron dissociation energies, but the absolute value of the thermo-kinetic parameter is always less than rather than greater than half of the absolute value of the electron affinity of the electron acceptor.

(6) For electron transfer reactions, when the electron donor and electron acceptor are changed, there is no fixed relationship between the change in the activation energy of the electron transfer reactions and the change in the thermodynamic driving forces of the electron transfer reactions because the activation free energy value of the electron transfer reactions is not only dependent on the thermodynamic driving forces of the electron transfer reactions but also dependent on the intrinsic barrier of the electron transfer reactions.

The greatest contribution of this paper is to realize the symmetry and unification of kinetic equations and the corresponding thermodynamic equations of electron transfer reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphyschemau.3c00001.

Prediction values for the activation free energies of 6900 electron transfer reactions in acetonitrile at 298 K (Table S1) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Xiao-Qing Zhu − *The State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China;* orcid.org/0000-0003-2785-640X; Email: xqzhu@nankai.edu.cn

Authors

Jin-Ye Zhang − *The State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China;* orcid.org/0000-0002-6028-2471

Li-Li Wang − *The State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsphyschemau.3c00001

Notes

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■ DEDICATION

Dedicated to the 60th anniversary of the Institute of Elemento-Organic Chemistry (Nankai University).

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