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I. Introduction

Hydride transfer is one of the most fundamental chemical processes.¹⁻⁹ The research on organic hydride transfer reactions has become a very important field of chemistry, because of their importance in chemical and biochemical reactions,10-14 wide applications to reducing unsaturated organic compounds¹⁵⁻²⁷ and the potential in hydrogen storage.²⁸⁻³⁰ There are two most fundamental scientific problems about the hydride transfer reactions (eqn (1)): one is the thermodynamic problem, *i.e.*, how to safely predict the thermodynamic driving forces of hydride transfer reactions ($\Delta G^{\circ} = ?$); the other is the kinetic problem, *i.e.*, how to reliably predict the activation energy of hydride transfer reactions ($\Delta G^{\neq} = ?$). As to the thermodynamic problem, as long as the free energy change of the hydride donor (XH) to release a hydride anion in solution $[\Delta G^{\circ}_{H^-D}(XH)]$ and the free energy change of the hydride acceptor (Y⁺) to capture a hydride anion in solution $[\Delta G^{\circ}_{H^{-}A}(Y^{+})]$ are available, this problem can be solved according to eqn (2).³¹ In fact, for many of the most important organic hydride donors, the free energy changes of them to release hydride anions in acetonitrile have been determined in

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A classical but new kinetic equation for hydride transfer reactions†

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A classical but new kinetic equation to estimate activation energies of various hydride transfer reactions was developed according to transition state theory using the Morse-type free energy curves of hydride donors to release a hydride anion and hydride acceptors to capture a hydride anion and by which the activation energies of 187 typical hydride self-exchange reactions and more than thirty thousand hydride cross transfer reactions in acetonitrile were safely estimated in this work. Since the development of the kinetic equation is only on the basis of the related chemical bond changes of the hydride transfer reactants, the kinetic equation should be also suitable for proton transfer reactions, hydrogen atom transfer reactions and all the other chemical reactions involved with breaking and formation of chemical bonds. One of the most important contributions of this work is to have achieved the perfect unity of the kinetic equation and thermodynamic equation for hydride transfer reactions.

our lab.³²⁻³⁵ Meanwhile, for many typical organic hydride acceptors, such as olefin, imine, quinone, carbonyl compounds, various organic cations etc., the free energy changes of them to capture hydride anions in acetonitrile have also been determined in our lab.^{36–38} It is true that for many important organic hydride transfer reactions in acetonitrile, the thermodynamic problems should have received good solutions.32-38 However, for hydride transfer reactions, the activation energy cannot be estimated reliably according to some related parameters of the reactants to date. The main reason is that the factors affecting the kinetics of hydride transfer reactions are much more complicated and diversified than those affecting the thermodynamics. In fact, no suitable theoretical approaches have been reported to date to accurately estimate the activation energy of hydride transfer reactions except that some research groups tried to apply Marcus theory for some hydride transfer reactions in a mixed solvent.39-44 Since Marcus theory was developed by Rudolph A. Marcus in 1956 for the outer sphere electron transfer reactions in solution⁴⁵ and has been identified to violate the law of conservation of energy,⁴⁶ it is necessary to develop a scientific method to estimate the activation energy of hydride transfer reactions. In this manuscript, a classical but new equation was introduced which can be used to safely estimate the activation energy of various hydride transfer reactions in acetonitrile. In fact, the kinetic equation developed in this work is not only suitable to estimate the activation energy of hydride transfer reactions but also suitable to estimate the activation energy of proton

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$$\mathbf{X}\mathbf{H} + \mathbf{Y}^+ \to \mathbf{X}^+ + \mathbf{Y}\mathbf{H} \tag{1}$$

$$\Delta G^{\circ} = \Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH}) + \Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{Y}^{+}) \tag{2}$$

II. Development of the kinetic equation for hydride transfer reactions

As is well known, for any hydride transfer reaction from hydride donors (**XH**) to hydride acceptors (**Y**⁺), the process of hydride transfer contains two chemical processes: one is the X-H bond dissociation for **XH** to release a hydride anion (H⁻), and the other is the Y-H bond formation for **Y**⁺ to capture the released hydride anion. According to transition state theory (TST),⁴⁷ the process of hydride transfer from **XH** to **Y**⁺ can be described by Scheme 1.

From Scheme 1, it is clear that the process of the hydride transfer from **XH** to **Y**⁺ may be regarded as two combined chemical processes: one is the dissociation of the X-H bond of **XH** to form **X**⁺ and **H**⁻ and the other is the formation of the Y-H bond of **Y**⁺ from **Y**⁺ and **H**⁻. Since the free energy changes of **XH** due to the X-H bond dissociation and of **Y**⁺ due to the Y-H bond formation from **Y**⁺ and **H**⁻ can be described using the Morse-type free energy curves (Fig. 1),^{48–51} the free energy change of the reaction system as the hydride transfers can be described by two different Morse-type free energy curves in the same reaction coordinate system and the free energy of **XH** at the ground state may be defined as zero (Fig. 2).

In Fig. 2, the left Morse-type curve describes the free energy changes of the species **XH** to release hydride anions, and the right one describes the free energy changes of the species \mathbf{Y}^+ to

$$(\widehat{\mathbf{X}})_{\text{HIMM}}(\widehat{\mathbf{H}}) + (\widehat{\mathbf{Y}}^{\dagger}) \rightleftharpoons \left[(\widehat{\mathbf{X}})_{\text{HIMM}}(\widehat{\mathbf{H}})_{\text{HIMM}}(\widehat{\mathbf{Y}}) \right]^{\dagger} \longrightarrow (\widehat{\mathbf{X}}^{\dagger}) + (\widehat{\mathbf{H}})_{\text{HIMM}}(\widehat{\mathbf{Y}})$$

 $\mbox{Scheme 1}$ The mechanism of hydride transfer from hydride donors (\mbox{XH}) to hydride acceptors $(\mbox{Y}^{\bullet}).$



Fig. 1 The dependence of the free energy change of the hydride donor (**XH**) to release a hydride anion on the internuclear separation can be described using the Morse-type free energy curve.



Fig. 2 The free energy changes of hydride transfer from **XH** to **Y**⁺ to form **X**⁺ and **YH** can be described by two different Morse-type free energy curves: the left one refers to the chemical process of **XH** to release a hydride anion; the right one refers to the chemical process of **Y**⁺ to capture **H**⁻.

capture hydride anions. The intersecting point of the two Morse-type free energy curves is just a symbol that the reaction of hydride transfer from XH to Y^+ has reached the transition state, because across the intersecting point of the two Morsetype curves, the sum of the state energy of the reaction system (**XH** and \mathbf{Y}^{+}) would change from an increase to a decrease as the hydride continues transfer. However, the free energy of the G-axis at the intersecting point is not the activation energy of the reactions, because the left Morse-type curve does not represent the reactants system. Since the left Morse-type curve in Fig. 2 is to describe the state free energy change of the hydride donor (XH), the right one is to describe the state free energy change of the hydride acceptor (\mathbf{Y}^{+}) , the activation free energy of the hydride transfer reaction should equal the sum of the absorbed free energy of the X-H bond due to the activation in the transition state, $\Delta G_{H^-D}^{\neq}(XH/Y^+)$, and the released free energy of the Y-H bond due to the formation in the transition state, $\Delta G_{H^-A}^{\neq}(Y^+/XH)$. In eqn (3), $\Delta G_{H^-D}^{\neq}(XH/Y^+)$ is called the X-H bond activation energy of XH in the transition state, and $\Delta G_{H^-A}^{\neq}(Y^+/XH)$ is called the Y–H bond formation energy of Y^+ in the transition state.

$$\Delta G^{\neq} = \Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{Y}^{+}) + \Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{Y}^{+}/\mathrm{XH})$$
(3)

From eqn (3) it is clear that for a hydride transfer reaction from **XH** to **Y**⁺ in solution, as long as the X–H bond activation energy of XH, $\Delta {\it G}_{{\rm H}^-{\rm D}}^{\neq}({\rm XH}/{\rm Y}^+),$ and the Y–H bond formation energy of \mathbf{Y}^{+} , $\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{Y}^{+}/\mathrm{XH})$, are available, the activation energy (ΔG^{\neq}) can be obtained by the addition of the two physical parameters, which is just like the derivation of the free energy change $(\Delta G^{\circ})^{31}$ of the reactions from the free energy change of **XH** to release a hydride anion $[\Delta G^{\circ}_{H^-D}(XH)]$ and the free energy change of $\boldsymbol{Y}^{\!\!+}$ to capture a hydride anion $[\Delta G^{\circ}_{H^-D}(Y^+)]$ (see eqn (2)). However, unlike $\Delta G^{\circ}_{H^-D}(XH)$, $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{Y}^{+})$ is not a characteristic parameter (constant) of the hydride donors (XH), because the magnitude of $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{Y}^{+})$ is not only dependent on the nature of XH, but also dependent on the nature of Y^+ . Similarly, $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{Y}^{+}/\mathrm{XH})$ is not a characteristic parameter (constant) of the hydride acceptors (Y^+) , either, since the magnitude of $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{Y}^{+}/\mathrm{XH})$ also depends on the nature of **XH**. Evidently, the strategy to derive the activation energy (ΔG^{\neq}) of hydride



Fig. 3 Relationships of four Morse-type free energy curves corresponding to the four partial reactions: $XH \rightarrow X^+ + H^-$ (bold line on the left), $Y^+ + H^- \rightarrow YH$ (bold line on the right), $YH \rightarrow Y^+ + H^-$ (dashed line on the left), and $X^+ + H^- \rightarrow XH$ (dashed line on the right).

transfer reactions using $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{Y}^{+})$ and $\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{Y}^{+}/\mathrm{XH})$ according to eqn (3) does not work.

In order to develop the direct dependence of the activation energy (ΔG^{\neq}) of hydride transfer reactions on the characteristic parameters of the two reactants themselves (**XH** and **Y**⁺), the geometrical relationship among the four intersecting points formed from the four Morse curves corresponding to the four related partial reactions (**XH** \rightarrow **X**⁺ + **H**⁻ and its inverse reaction as well as **Y**⁺ + **H**⁻ \rightarrow **YH** and its inverse reaction) was examined in Fig. 3. The result clearly shows that for the general hydride transfer reactions with the type of **XH** + **Y**⁺ \rightarrow **X**⁺ + **YH**, the sum of $\Delta G^{\neq}_{\mathrm{H}^-\mathrm{D}}(\mathrm{XH}/\mathrm{Y}^+)$ and $\Delta G^{\neq}_{\mathrm{H}^-\mathrm{A}}(\mathrm{Y}^+/\mathrm{XH})$ should be equal to or quite close to the sum of $\Delta G^{\neq}_{\mathrm{H}^-\mathrm{D}}(\mathrm{XH}/\mathrm{X}^+)$ and $\Delta G^{\neq}_{\mathrm{H}^-\mathrm{A}}(\mathrm{Y}^+/\mathrm{YH})$. Thus, eqn (3) can be replaced by eqn (4).

$$\Delta G^{\neq} = \Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{X}^{+}) + \Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{Y}^{+}/\mathrm{YH}) \tag{4}$$

In eqn (4), $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH}/\mathrm{X}^{+})$ [abbreviated as $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})$ below] is the X-H bond activation energy of XH at the transition state for the hydride self-exchange reaction of XH with \mathbf{X}^{+} ($\mathbf{X}\mathbf{H} + \mathbf{X}^{+} \rightarrow \mathbf{X}\mathbf{H} + \mathbf{X}^{+}$), *i.e.*, the energy that the hydride donor XH absorbs when the reaction proceeds from the initial state to the transition state. $\Delta G_{H^-A}^{\neq}(Y^+/YH)$ [abbreviated as $\Delta G_{H^-A}^{\neq}(Y^+)$ below] is the Y-H bond formation energy of Y^+ at the transition state for the hydride self-exchange reaction of Y⁺ with **YH** ($\mathbf{Y}^+ + \mathbf{YH} \rightarrow \mathbf{YH} + \mathbf{Y}^+$), *i.e.*, the energy that the hydride acceptor Y^{+} releases when the reaction proceeds from the initial state to the transition state. Since X^{+} is the conjugate cation of XH, the nature of X^+ should depend on that of the corresponding hydride donors XH, which indicates that $\Delta G_{H^-D}^{\neq}(XH)$ like $\Delta G_{H^-D}^{\circ}(XH)$ is also one of characteristic parameters of hydride donors (XH), i.e., the magnitude of $\Delta G_{\mathrm{H}^-\mathrm{D}}^{\neq}(\mathrm{XH})$ only depends on the nature of **XH**. Similarly, $\Delta G^{\neq}_{H^-A}(Y^+)$ like $\Delta G^{^\circ}_{H^-A}(Y^+)$ is also one of the characteristic parameters of the hydride acceptor (Y^+) , *i.e.*, the magnitude of $\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{Y}^{+})$ only depends on the nature of Y^{+} . Thus, if the characteristic parameters $\Delta G_{H^-D}^{\neq}(XH)$ of various hydride donors (**XH**) and $\Delta G_{H^-A}^{\neq}(\mathbf{Y}^+)$ of various hydride acceptors (**Y**⁺) in solution are available, the activation energies of various hydride transfer reactions (including hydride self-exchange

reactions and hydride cross transfer reactions) can be derived from eqn (4).

III. Determination of $\Delta G_{H^-D}^{\neq}(XH)$ and $\Delta G_{H^-A}^{\neq}(Y^+)$ and the results in acetonitrile

According to eqn (4), it is clear that if $\Delta G_{H^-D}^{\neq}(XH)$ of various hydride donors **XH** in solution and $\Delta G_{H^-A}^{\neq}(Y^+)$ of various hydride acceptors **Y**⁺ in solution are available, the activation energy of various hydride transfers from hydride donors (**XH**) to hydride acceptors (**Y**⁺) in the solution can be estimated, so it is necessary to determine $\Delta G_{H^-D}^{\neq}(XH)$ and $\Delta G_{H^-A}^{\neq}(X^+)$ of various hydride donors **XH** and their corresponding salts (**X**⁺) in solution.

For the hydride self-exchange reaction: $XH + X^{+} \rightarrow X^{+} + XH$, since

$$\Delta G^{\neq}(\mathbf{X}\mathbf{H}/\mathbf{X}^{+}) = \Delta G^{\neq}_{\mathbf{H}^{-}\mathbf{D}}(\mathbf{X}\mathbf{H}) + \Delta G^{\neq}_{\mathbf{H}^{-}\mathbf{A}}(\mathbf{X}^{+})$$
(5)

and

$$\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{X}^{+}) = \Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{X}\mathrm{H}) + \Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\circ}(\mathrm{X}^{+}) \tag{6}$$

so

$$\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{X}\mathrm{H}) = 1/2[\Delta G^{\neq}(\mathrm{X}\mathrm{H}/\mathrm{X}^{+}) - \Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\circ}(\mathrm{X}^{+})]$$
(7)

From eqn (7), it is conceived that for a hydride self-exchange reaction, as long as the activation energy of the hydride self-exchange reaction, $\Delta G^{\neq}(\text{XH}/\text{X}^{+})$, can be determined, $\Delta G_{\text{H}^{-}\text{D}}^{\neq}(\text{XH})$ can be obtained from eqn (7), because the free energy change of the many important hydride acceptors (\mathbf{X}^{+}) in solution [$\Delta G_{\text{H}^{-}\text{A}}^{\circ}(\text{X}^{+})$] has been obtained in our lab.^{33–38} Thus, the remaining work is just to determine the activation energies $\Delta G^{\neq}(\text{XH}/\text{X}^{+})$ of various hydride self-exchange reactions in solution.

As is well known, for electron or proton self-exchange reactions, the activation energy of the reactions can be determined using dynamic EPR and dynamic NMR techniques, since the rates of electron and proton self-exchange reactions are generally fast enough to meet the criteria of the dynamic EPR and dynamic ¹H NMR measurements [k_2 (self-exchange) within 10^2-10^6 M⁻¹ s⁻¹].⁵² But for hydride self-exchange reactions, the dynamic NMR method cannot be applied to determine the activation energy of the reactions, because the rates of hydride self-exchange reactions are quite slow, generally much smaller than 1×10^2 M⁻¹ s⁻¹. In fact, no effective experimental method has been reported to determine the rates of hydride selfexchange reactions in solution.

Although direct experimental determination of the activation energies of hydride self-exchange reactions in solution is impossible, the activation energies of the hydride cross transfer reactions $(XH + Y^+ \rightarrow X^+ + YH, X \neq Y)$ generally can be determined using conventional experimental techniques as long as the thermodynamic driving forces of the hydride cross transfer reactions are appropriate. This fact induces us to develop a method to estimate the activation energies of



Scheme 2 Structures of three well-chosen organic hydride donors and the corresponding cations.

various hydride self-exchange reactions in solution according to the activation energies of the related hydride cross transfer reactions. In order to determine $\Delta G_{H^-D}^{\neq}(XH)$ of the various hydride donors (**XH**) in acetonitrile and establish the data library, **A**₁**H**, **A**₂**H** and **A**₃**H** in Scheme 2 were carefully chosen as three typical organic hydride donors to construct three different hydride cross transfer reactions (eqn (8)–(10)).

$$\mathbf{A_1H} + \mathbf{A_2}^+ \to \mathbf{A_1}^+ + \mathbf{A_2H} \tag{8}$$

$$\mathbf{A_1H} + \mathbf{A_3}^+ \to \mathbf{A_1}^+ + \mathbf{A_3H}$$
(9)

$$\mathbf{A_2H} + \mathbf{A_3}^+ \to \mathbf{A_2}^+ + \mathbf{A_3H} \tag{10}$$

According to eqn (8)-(10), the three eqn (11)-(13) can be derived from eqn (4) by introducing eqn (6).

$$\begin{split} \Delta G^{\neq}({\rm A_{1}H/A_{2}}^{+}) &= \Delta G^{\neq}_{{\rm H^{-}D}}({\rm A_{1}H}) + \Delta G^{\neq}_{{\rm H^{-}D}}({\rm A_{2}H}) \\ &+ \Delta G^{\circ}_{{\rm H^{-}A}}({\rm A_{2}}^{+}) \end{split} \tag{11}$$

$$\Delta G^{\neq}(\mathbf{A}_{1}\mathbf{H}/\mathbf{A}_{3}^{+}) = \Delta G^{\neq}_{\mathbf{H}^{-}\mathbf{D}}(\mathbf{A}_{1}\mathbf{H}) + \Delta G^{\neq}_{\mathbf{H}^{-}\mathbf{D}}(\mathbf{A}_{3}\mathbf{H}) + \Delta G^{\circ}_{\mathbf{H}^{-}\mathbf{A}}(\mathbf{A}_{3}^{+})$$
(12)

$$\Delta G^{\neq}(A_{2}H/A_{3}^{+}) = \Delta G^{\neq}_{H^{-}D}(A_{2}H) + \Delta G^{\neq}_{H^{-}D}(A_{3}H) + \Delta G^{\circ}_{H^{-}A}(A_{3}^{+})$$
(13)

In eqn (11)–(13), $\Delta G^{\neq}(A_1H/A_2^+)$, $\Delta G^{\neq}(A_1H/A_3^+)$ and $\Delta G^{\neq}(A_2H/A_3^+)$ are the activation energies of the three hydride cross transfer reactions (eqn (8)–(10)) in acetonitrile, respectively, which can be directly derived from the corresponding rate constants at 298 K according to the Eyring equation; the



Fig. 4 Profile of the UV-vis absorbance of A_3^+ at $\lambda_{max} = 495$ nm during the hydride transfer from A_2H to A_3^+ (G = p-CH₃O). Conditions: 0.12 mM A_3^+ , 3.15 mM A_2H in dry acetonitrile at 298 K.

XH	\mathbf{Y}^{+}	$\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+})$ a	$\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{Y}^{+})$ ^a	$\Delta G^{\neq b}$
A1H	$egin{array}{c} A_2^{\ +} \ A_3^{\ +} \ A_3^{\ +} \ A_3^{\ +} \end{array}$	-66.4	-76.2	17.9
A1H		-66.4	-90.2	12.6
A2H		-76.2	-90.2	14.5

^{*a*} Derived from experimental measurements using ITC or HPLC, the unit is kcal mol⁻¹, and the uncertainty is smaller than 0.5 kcal mol⁻¹. ^{*b*} Derived from experimental measurements using a stopped-flow UV-vis spectrometer; the uncertainty is smaller than 0.1 kcal mol⁻¹.

latter were determined by the stopped-flow UV-vis method (see Fig. 4); $\Delta G^{\circ}_{H^-A}(A_2^+)$ and $\Delta G^{\circ}_{H^-A}(A_2^+)$ are the free energies of the hydride acceptors A_2^+ and A_3^+ to capture the hydride anion in acetonitrile at 298 K, respectively, which can be derived from experimental measurements using ITC or HPLC.⁵³

Table 1 lists the free energy change values of the three hydride acceptors $(A_1^+, A_2^+ \text{ and } A_3^+)$ to capture hydride anions in acetonitrile at 298 K and the activation energies of the three hydride cross transfer reactions (eqn (8)–(10)) in acetonitrile at 298 K.

By examining eqn (11)-(13), it is found that eqn (11)-(13) contain three isolated variables: $\Delta G_{\rm H^-D}^{\neq}(A_1{\rm H})$, $\Delta G_{\rm H^-D}^{\neq}(A_2{\rm H})$ and $\Delta G_{\rm H^-D}^{\neq}(A_3{\rm H})$. If the three eqn (11)-(13) are treated together to get a simultaneous solution after substituting the known data in Table 1 into the equations, the X-H bond activation energies of the three hydride donors (A₁H, A₂H and A₃H) for their hydride self-exchange reactions (eqn (14)-(16)) in acetonitrile at 298 K can all be obtained at the same time. The result is that $\Delta G_{\rm H^-D}^{\neq}(A_1{\rm H}) = 46.1$ kcal mol⁻¹ for A₁H (eqn (14)), $\Delta G_{\rm H^-D}^{\neq}(A_3{\rm H}) = 56.7$ kcal mol⁻¹ for A₃H (eqn (16)) in acetonitrile at 298 K.

$$\mathbf{A_1H} + \mathbf{A_1}^+ \to \mathbf{A_1}^+ + \mathbf{A_1H}$$
(14)

$$\mathbf{A_2H} + \mathbf{A_2}^+ \to \mathbf{A_2}^+ + \mathbf{A_2H} \tag{15}$$

$$\mathbf{A_3H} + \mathbf{A_3}^+ \to \mathbf{A_3}^+ + \mathbf{A_3H}$$
(16)

Since \mathbf{A}_2^+ is a strong hydride acceptor and $\Delta G_{\mathrm{H}^-\mathrm{D}}^+(\mathbf{A}_2\mathbf{H})$ (48.0 kcal mol⁻¹) and $\Delta G_{\mathrm{H}^-\mathrm{A}}^\circ(\mathbf{A}_2\mathbf{H})$ (-76.2 kcal mol⁻¹)^{35b} have been determined, it is not difficult to get $\Delta G_{\mathrm{H}^-\mathrm{D}}^{\neq}(\mathbf{XH})$ of any another hydride donor (**XH**) in solution according to eqn (11) by constructing a hydride cross transfer reaction with \mathbf{A}_2^+ (eqn (17)). In this work, the second order rate constants (k_2) at 298 K and the corresponding activation energies of 187 typical hydride cross transfer reactions in acetonitrile were determined, and the detailed results are summarized in Table 2. In order to examine the dependence of ΔG^{\neq} on ΔG° for the hydride transfer reactions and the effect of the free energy changes of the hydride transfer reactions (ΔG°) on the $\Delta G_{\mathrm{H}^-\mathrm{D}}^+(\mathrm{XH})$, as well as the relationship between $\Delta G_{\mathrm{H}^-\mathrm{D}}^+(\mathrm{XH})$ and $\Delta G_{\mathrm{H}^-\mathrm{D}}^\circ(\mathrm{XH})$, the free energy changes (ΔG°) of the 187 typical hydride cross transfer reactions from **XH** to **Y**⁺ in

Table 2 Second-order rate constants (k_2) and molar free energy changes (ΔG°) of the hydride transfer from **XH** to **Y**⁺ or to **Y**⁺ from **XH** in acetonitrile at 298 K together with the corresponding reaction activation energies (ΔG^{\neq}) and the X–H bond activation free energies [$\Delta G^{\neq}_{H^-D}(XH/Y^+)$]

No.	Hydride donors or	acceptors	k_2^{a}	$\Delta G^{\neq b}$	$\Delta G^{\circ c}$	$[\Delta G^{ eq}_{\mathrm{H}^-\mathrm{D}}(\mathrm{XH}/\mathrm{Y}^+)]^d$
$1H^e$		R = Me	1.65	17.15	-16.7	40.67
		Et	2.04	17.02	-16.9	40.51
		ⁱ Pr	1.15	17.36	-16.9	40.68
	Gharm	^t But	8.30×10^{-3}	20.28	-16.9	42.13
		Bn	2.20	16.98	-16.9	40.48
		Ph	1.30×10^{-1}	18.65	-17.0	41.27
$2\mathbf{H}^{e}$		G = p-MeO	$9.70 imes 10^1$	14.73	-18.0	38.81
		<i>p</i> -Me	$8.36 imes 10^1$	14.82	-17.5	39.11
	N CH-Ph(G)	<i>р</i> -Н	$7.61 imes 10^1$	14.88	-16.9	39.44
		p-F	$7.16 imes 10^1$	14.91	-16.8	39.50
		<i>p</i> -Cl	$5.16 imes 10^1$	15.11	-16.1	39.95
	нн	p-CN	2.58×10^{1}	15.52	-14.8	40.81
$3H^e$	сосн3	G = p-MeO	2.55×10^{1}	15.53	-14.9	40.76
		<i>p</i> -Ме	$2.38 imes 10^1$	15.57	-14.6	40.93
	N CH-Pb(G)	<i>р</i> -Н	$1.77 imes 10^1$	15.74	-14.0	41.32
	0.121 ((0))	p-F	1.49×10^{1}	15.84	-13.9	41.42
		<i>p</i> -Cl	$1.28 imes 10^1$	15.93	-13.5	41.66
		p-CN	9.81	16.09	-12.1	42.44
$4\mathbf{H}^{e}$	со2сн3	G = p-MeO	$4.18 imes 10^1$	15.23	-16.2	39.96
		<i>p</i> -Ме	3.80×10^{1}	15.29	-15.9	40.14
	N CH₂Ph(G)	<i>р</i> -Н	$3.10 imes 10^1$	15.41	-15.3	40.50
		p-F	$2.45 imes 10^1$	15.55	-15.2	40.62
		<i>p</i> -Cl	$2.17 imes 10^1$	15.62	-14.5	41.01
	нн	p-CN	9.91	16.09	-13.2	41.89
$5H^e$	сно	G = p-MeO	8.42×10^{-1}	17.55	-11.4	43.52
		<i>p</i> -Ме	7.71×10^{-1}	17.60	-11.0	43.74
	N CH₂Ph(G)	<i>р</i> -н	5.97×10^{-1}	17.75	-10.6	44.02
		p-F	5.18×10^{-1}	17.83	-10.6	44.06
	н н	<i>p</i> -CN	2.38×10^{-1}	18.29	-8.5	45.34
$\mathbf{6H}^{e}$	CN	G = p-MeO	6.68×10^{-1}	17.68	-10.9	43.84
		<i>p</i> -Me	6.41×10^{-1}	17.71	-10.5	44.05
	CH ₂ Ph(G)	<i>р</i> -н	4.55×10^{-1}	17.91	-9.8	44.50
	- • •	p-F	3.32×10^{-1}	18.10	-9.7	44.64
		<i>p</i> -Cl	1.61×10^{-1}	18.52	-8.7	45.36
	нн	<i>p</i> -CN	9.20×10^{-2}	18.86	-7.2	46.27
$\mathbf{7H}^{e}$	CONH ₂	R = Me	2.88×10^{2}	14.09	-20.4	37.29
		Et	2.38×10^{2}	14.20	-19.6	37.75
	R	¹ Pr	1.02×10^{2}	14.70	-20.3	37.65
	нн	ⁿ But	3.43×10^{2}	13.99	-19.8	37.54
$\mathbf{8H}^{e}$	CO₂H		$2.58 imes 10^{1}$	15.52	-13.6	41.41
	N N					
oute	CH2Ph HH		0.04401	14.00	17.0	20.24
9H ²	CONHEt		8.34×10^{-5}	14.82	-17.3	39.21
	L N					
	CH ₂ Ph					
1011 ⁰	ң н		1.20×10^{1}	15.01	15.0	40.45
10H	CONHPh		4.38 × 10	15.21	-15.2	40.45
	[∥] N [−]					
	CH ₂ Ph					
11 U ^e	н_н		1.00×10^4	11.61	_20.1	32.20
1111	\square		1.90 ~ 10	11.01	-20.1	32.20
	N N					
	ĊH ₂ Ph					
12H ^e	H H CH-		2.61×10^4	11 42	-33.1	29.61
1211	f Yong		2.01 . 10	11.12	00.1	25:01
	N N					
	ĊH ₂ Ph					
$13H^{e}$	H ₂ C, H H .CONH ₂		9.13×10^{1}	14.77	-19.6	38.03
	N N					
	CH ₂ Ph					
$14H^e$			1.65	17.15	-12.9	42.57
	'N' I CH₂Ph					

Table 2 (Contd.)

No.	Hydride donors or acc	ceptors	$k_2^{\ a}$	$\Delta G^{\neq b}$	$\Delta G^{\circ c}$	$[\Delta G^{ eq}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH}/\mathrm{Y}^{+})]^{d}$
15H ^e		G = n - MeO	1.23×10^{1}	15.96	-14.3	41.27
	Γ Ύ	n-Me	8.35	16.19	-13.6	41.74
	N	р 1.10 n-H	4.62	16 54	-12.3	42.56
	Ph(G)	p-fi p-Cl	1.66	17 14	-10.9	43 57
		<i>p</i> -Br	1.57	17.14	-10.7	43.68
16 U ^e	CONH ₂	p DI G = p MeO	1.06×10^{1}	16.05	-15.7	40.62
1011	H	G = p-MeO	6.00	16.05	-13.7	40.02
		<i>p</i> -Me	8.00	10.38	-15.1	41.09
	FII(G)	p-H	3.63	16.68	-13.8	41.89
		p-Cl	1.02	17.43	-12.1	43.11
	нн	<i>p</i> -Br	1.02	17.43	-12.0	43.16
$17H^{e}$	EtO2C CO2Et		1.68×10^{2}	14.41	-11.8	41.75
	H ₃ C CH ₃					
$18H^e$			2.18	16.98	-12.0	42.94
	H ₃ C N CH ₃					
19H ^e			0.52	17.83	-5.3	46.71
$20H^e$	NO ₂		3.02	16.79	-7.2	45.24
	H H CH3					
a da se	ÇH₃	a	0.04 2	10.15	a - -	21.00
21H ^c	N H	$G = p - NMe_2$	9.24×10^{2}	13.40	-30.5	31.90
	Ph(G)	<i>p</i> -MeO	3.05×10^{2}	14.06	-28.2	33.37
	CH ₃	<i>р</i> -Ме	2.42×10^2	14.19	-27.7	33.69
	•	<i>р</i> -Н	$1.77 imes 10^2$	14.38	-27.0	34.14
		p-Cl	$7.54 imes 10^1$	14.88	-25.9	34.94
		$p-CF_3$	$4.29 imes 10^1$	15.22	-24.6	35.76
		<i>p</i> -CN	2.59×10^{1}	15.52	-24.4	36.00
		<i>p</i> -NO ₂	1.80×10^{1}	15.73	-24.0	36.31
		$p \operatorname{IO}_2$	1.56×10^2	14.45	_29.5	22.42
		<i>p</i> -OH	1.30×10^{2}	14.45	-26.3	33.42
		0-0H	1.56 × 10	14.45	-27.3	34.02
		o-Me	/.21	16.27	-29.7	33./3
	CH ₃	o-Cl	1.56×10^{2}	14.45	-27.9	33.72
22H ^c	K H		1.08×10^{3}	13.31	-31.6	31.30
0	сн ₃ сн ₃		-2			
$23H^{e}$	N	G = p-MeO	3.84×10^{-2}	19.37	-23.3	38.48
	N-CH ₃	<i>p</i> -Me	2.72×10^{-2}	19.58	-23.0	38.73
	H Ph(G)	<i>р</i> -Н	2.17×10^{-2}	19.71	-22.5	39.05
		<i>p</i> -Br	1.09×10^{-2}	20.12	-21.7	39.65
		p-CF ₃	0.49×10^{-2}	20.59	-20.7	40.39
$24H^e$		1 - 5	1.16×10^{-1}	18.72	-27.4	36.10
	H H					
25H ^e	н '' О сн _з		9 24 $\times 10^{1}$	14 76	-23 5	36.08
2511			3.24 × 10	14.70	25.5	50.00
26H ^e	сн ₃ сн ₃		6.20×10^{1}	15.00	-21.9	37.00
2011	HN ^N N H CH ₃ CH ₃		0.20 ^ 10	13.00	-21.7	57.00
$27 H^i$	H H CH3		3.21	16.75	-10.5	43.57
$\mathbf{28H}^{f}$	H H CONH2		$3.78 imes 10^4$	11.20	-16.5	45.50
29H ^{<i>f</i>}	$\sqrt{2}$		$2.77 imes 10^2$	14.11	-16.2	47.10
	∕ ° _⊖ ∕					

No.	Hydride donors or a	cceptors	k2 a	$\Delta G^{\neq b}$	$\Delta G^{\circ c}$	$[\Delta G^{ eq}_{\mathrm{H}^-\mathrm{D}}(\mathrm{XH}/\mathrm{Y}^+)]^d$
30H ^f	H Ph(G)	G = p-MeO	$5.01 imes 10^3$	12.40	-23.3	42.70
	$\left(\right)$	<i>p</i> -Me	3.85×10^3	12.55	-22.7	43.07
	N Ph	р-н	$2.55 imes 10^3$	12.80	-21.7	43.70
	Ph	<i>p</i> -Br	$1.19 imes 10^3$	13.25	-20.3	44.62
		<i>p</i> -Cl	$1.28 imes 10^3$	13.21	-20.8	44.35
		<i>m</i> -Cl	0.93×10^{3}	13.40	-20.0	44.85
$1 H^{f}$	L H Ph	G = p-MeO	$3.56 imes 10^3$	12.60	-23.8	42.55
		<i>p</i> -Me	$3.23 imes 10^3$	12.66	-22.6	43.18
		<i>p</i> -Br	$1.50 imes 10^3$	13.11	-19.7	44.85
	Pn	p-Cl	$1.37 imes 10^3$	13.17	-20.4	44.53
	2	<i>m</i> -Cl	$0.99 imes 10^3$	13.36	-18.7	45.48
$2\mathbf{H}^{f}$	Ŭ H ∕ Ph	G = p-MeO	$3.88 imes 10^3$	12.55	-22.2	43.32
	$(\uparrow \uparrow \uparrow)$	<i>p</i> -Me	$2.97 imes 10^3$	12.71	-22.0	43.50
	N Ph	<i>p</i> -Br	$1.24 imes 10^3$	13.23	-21.1	44.21
	Ph(G)	p-Cl	$1.27 imes 10^3$	13.21	-21.2	44.15
		<i>m</i> -Cl	$0.92 imes 10^3$	13.40	-20.8	44.45
3H ^f	H H		4.76×10^{1}	15.16	-19.0	46.22
	0 OPh					
$\mathbf{4H}^{f}$	H		9.50×10^{-1}	17.47	-21.7	46.03
F	O OPh H Ph(G)					
$5H^J$		G = p-MeO	4.17×10^{-1}	17.96	-17.8	48.23
	i	<i>p</i> -Me	3.73×10^{-1}	18.03	-17.5	48.41
	CH ₃ CH ₃	<i>р</i> -Н	3.51×10^{-1}	18.06	-18.8	47.78
		<i>p</i> -Cl	3.10×10^{-1}	18.14	-17.0	48.71
		p-NO ₂	2.23×10^{-1}	18.33	-16.3	49.16
6H ^g	MeO ₂ C CO ₂ Me	G = p-MeO	$2.59 imes 10^3$	12.79	-37.4	40.39
		<i>p</i> -Me	$1.81 imes 10^3$	13.00	-37.0	40.70
	H ₃ C N CH ₃	р-Н	$1.53 imes 10^3$	13.10	-36.4	41.05
	0.13	p-Cl	$6.22 imes 10^2$	13.63	-35.2	41.91
	11	p-CF ₃	$2.79 imes 10^2$	14.11	-33.9	42.80
87 H ^g	EtO ₂ C Ph(G) CO ₂ Et	G = p-MeO	$4.38 imes 10^3$	12.48	-38.6	39.64
	II	<i>p</i> -Me	$3.35 imes 10^3$	12.64	-38.1	39.97
	H ₃ C N CH ₃	p-H	$2.20 imes 10^3$	12.89	-37.5	40.39
	Ch3	p-Cl	9.36×10^{2}	13.39	-36.0	41.39
		p-CF ₂	3.60×10^{2}	13.96	-34.7	42.33
8H ^g	[/] PrO₂C, H Ph(G) _CO₂ [/] Pr	G = p-MeO	$3.98 imes 10^3$	12.54	-40.4	38.76
	T T	<i>p</i> -Me	$2.04 imes 10^3$	12.93	-39.9	39.21
	H ₃ C N CH ₃	p-H	1.47×10^{3}	13.12	-39.0	39.76
	CH ₃	p-Cl	5.87×10^{2}	13.67	-37.1	40.98
		<i>p</i> -CF ₂	2.45×10^{2}	14.19	-35.4	42.09
9H ^g		P = H	2.34×10^{3}	12.85	-35.7	41.27
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		Me	3.51×10^{3}	12.60	-37.5	40.25
	H ₃ C ^N CH ₃	Et	4.75×10^3	12.43	-38.4	39.71
nug	Ph(G)	$G = n M_{CO}$	2.70×10^{5}	0.04	10.0	27.60
OH	MeO ₂ C CO ₂ Me	G = p-MeO	3.78×10	9.84	-40.0	37.62
	H ₃ C N CH.	<i>p</i> -Me	3.31×10^{-10}	9.92	-39./	37.81
	CH ₃	<i>p</i> -н т С	2.99×10^{-1}	9.98	-39.3	38.04
		p-CI	$1./3 \times 10^{-5}$	10.30	-38./	38.50
4770	Ph(G)	p-CF ₃	1.09 × 10	10.57	-37.8	39.09
1H°	EtO ₂ C CO ₂ Et	G = p-MeO	4.06×10^{-10}	9.80	-40.4	37.40
	H ₃ C N CH.	<i>р</i> -ме	3.50×10^{-10}	9.88	-40.2	37.54
	CH ₃	р-н	3.12×10^{-5}	9.95	-39.8	37.77
		p-CI	1.81×10^{5}	10.27	-39.0	38.34
a	Ph(G)	p-CF ₃	1.15×10^{-5}	10.54	-38.1	38.92
$2H^{s}$	[/] PrO ₂ C CO ₂ [/] Pr	G = p-MeO	3.22×10^{-5}	9.93	-40.9	37.22
	Н	<i>p</i> -Me	2.81×10^{5}	10.01	-40.7	37.36
	H3C N CH3 CH4	<i>р</i> -н	2.29×10^{5}	10.14	-40.4	37.57
	0.13	<i>p</i> -Cl	1.56×10^{5}	10.36	-39.6	38.08
	В	p-CF ₃	9.81×10^{4}	10.64	-38.6	38.72
$3H^g$	EtO ₂ C	R = H	1.44×10^5	10.41	-37.3	39.25
	T LH	Me	$1.45 imes 10^6$	9.04	-42.6	35.92
	H ₃ C N CH ₃ CH ₃	Et	$9.85 imes 10^5$	9.27	-41.5	36.58
$4\mathbf{H}^h$	CH ₂ Ph(G)	G = p-MeO	$4.21 imes 10^2$	13.87	-23.4	40.68
		<i>p</i> -Me	$3.53 imes 10^2$	13.97	-22.5	41.18
		р-Н	$2.95 imes 10^2$	14.08	-21.7	41.63
	H ₂ N ¹⁰	<i>p</i> -F	$2.66 imes 10^2$	14.14	-21.2	41.92
	N CH₂Ph(G)					

Table 2 (Contd.)

No.	Hydride donors or	acceptors	k_2^{a}	$\Delta G^{\neq \ b}$	$\Delta G^{\circ c}$	$[\Delta G^{ eq}_{\mathrm{H^{-}D}}(\mathrm{XH}/\mathrm{Y^{+}})]^{d}$
45H ^{<i>i</i>}	H Ph(G)	G = p-MeO	25.57×10^{2}	12.80	-29.2	42.05
	N Cons	<i>p</i> -Me	23.09×10^{2}	12.86	-28.1	42.63
		p-H	17.26×10^{2}	13.03	-27.5	43.02
		p-Cl	$9.11 imes 10^2$	13.41	-26.4	43.76
		$p-CF_3$	$2.86 imes 10^2$	14.09	-24.7	44.95
46H ^{<i>i</i>}	H H	1 - 5	$4.68 imes 10^4$	11.08	-13.0	49.19
$47H^i$			$1.81 imes 10^1$	15.73	-26.0	45.01
	H ₃ C N CH ₃					
48 ^{+j}	Ph(G)	G = n-MeO	6.81×10^{-1}	17.67	-13.6	
10		n-Me	8.92×10^{-1}	17 51	-14.2	
	Ph	<i>p</i> -H	1.77	17.11	-16.2	
	•	p-ri p-Cl	3 35	16.73	-18.9	
		<i>p</i> -CF ₂	1.15×10^{1}	16.00	-22.5	
49 ^{+j}	Ph(G)	G = n - Me O	6.87×10^{-1}	17.67	-12.4	
15		n-Me	9.13×10^{-1}	17.57	-13.5	
	N N N	n-H	9.60×10^{-1}	17.00	-14.8	
	ĊH ₃	p-ri p-Cl	1 58	17.17	-16.5	
		<i>p</i> -CF ₂	2.04	17.17	-19.1	
50 ^{+k}	Ph(G)	G = n - Me O	1.73×10^{1}	15.76	-16.7	
00	S [⊕]	n-Me	453×10^{1}	15.19	-17.6	
		p-H	6.63×10^{1}	14.96	-18.1	
		p II p-Cl	1.11×10^2	14.50	-19.0	
		p-CF-	1.87×10^{2}	14 35	-20.5	
51 ^{+k}	H I	p or 3	4.68×10^4	11.08	-19.4	
01			1.00 . 10	11.00	13.1	
52 ^{+k}	⊕ Ph(G)	G = n MeO	2.21×10^2	14.25	_17 3	
32		n - Me	3.24×10^2	14.23	-12.1	
	s s	p-Mc	3.24×10^{2}	12.06	-10.0	
	Φ	p-11 p-Cl	5.01×10^{2}	13.90	-19.8	
		p-CF	6.93×10^2	13.75	-21.4	
53 ^{+l}	Ph(G)	$p - Gr_3$ G = n - MeO	1.67×10^4	11.60	-24.1	
55	$\bigwedge \land \land$	n - Me	2.14×10^4	11.09	-20.9	
		p-Wic n-H	2.14×10^{4}	11.34	-20.9	
	æ	p II p-Cl	6.62×10^4	10.87	-22.8	
		<i>p</i> OI <i>n</i> -Br	6.02×10^{4}	10.07	-23.8	
		<i>p</i> DI <i>n</i> -CF-	1.14×10^5	10.51	-22.1	
		<i>p</i> OI 3 <i>m</i> -MeO	4.94×10^{4}	11.04	-21.6	
		<i>m</i> -Me	3.06×10^4	11.04	-23.4	
		m-CE-	9.78×10^4	10.64	-25.9	
54 ^{+m}	N N	m Gr ₃	1.97×10^{2}	14 31	-23.3	
54	CH ₂		1.57 ~ 10	14.51	-22.5	
55 ⁺ⁿ	H		9.13×10^{-1}	17 50	-11.0	
JJ			5.13 ^ 10	17.50	-11.0	
- c ⁺⁰	CH ₂ Ph NHCOCH ₃		a co4			
56	H ₃ C		2.69×10^{4}	11.40	-26.6	
	H ₃ C N CH ₃					

^{*a*} k_2 is the second-order rate constant of the hydride transfer in acetonitrile at 298 K. The data of k_2 (M⁻¹ s⁻¹) were obtained from experimental measurements by the UV-vis method. The uncertainty is smaller than 5%. ^{*b*} Derived from the Eyring equation (T = 298 K); the unit is kcal mol⁻¹. ^{*c*} Derived from the corresponding reaction heats, because for the hydride transfer reactions with the type of **XH** + **Y**⁺ \rightarrow **X**⁺ + **YH**, the free energy change of the reactions in acetonitrile (ΔG°) has been verified to be equal to or quite close to the corresponding reaction heat (see ESI).³¹ The latter were directly derived from experimental measurements by ITC. The reproducibility is ±0.5 kcal mol⁻¹. ^{*d*} $\Delta G^{\neq}_{H^-D}(XH/Y^+)$ were derived from the corresponding ΔG^{\neq} and $\Delta G^{\circ}_{H^-D}(XH)$ according to eqn (7). The unit is kcal mol⁻¹. ^{*e*} To react with 10-methylacridinium (**46**⁺) in acetonitrile at 298 K. ^{*f*} To react with 9-phenylxanthylium [**53**⁺ (G = *p*-H)] in acetonitrile at 298 K. ^{*g*} To react with 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium (**56**⁺) in acetonitrile at 298 K. ^{*h*} To react with 1-benzyl-1,4-dihydronicotinamide [**2H** (G = *p*-H)] in acetonitrile at 298 K. ^{*k*} To react with 10-methyl-9,10-dihydronicotinamide acetate (**28H**) in acetonitrile at 298 K. ^{*m*} To react with 1-benzyl-1,4-dihydronicotinamide [**15H** (G = H)] in acetonitrile at 298 K. ^{*n*} To react with 1-benzyl-1,4-dihydronicotinamide [**49H** (G = H)] in acetonitrile at 298 K.

acetonitrile at 298 K were determined. The detailed results are also summarized in Table 2.

$$\mathbf{X}\mathbf{H} + \mathbf{A}_{2}^{+} \xrightarrow{\Delta G^{\ddagger}(\mathbf{X}\mathbf{H}/\mathbf{A}_{2}^{+})}_{\mathrm{CH}_{3}\mathrm{CN}} \mathbf{X}^{+} + \mathbf{A}_{2} \mathbf{H}$$
(17)

From the related data in Table 2, the values of $\Delta G_{H^-D}^{\neq}(XH)$ of the 187 hydride donors (**XH**) for their hydride self-exchange reactions in acetonitrile at 298 K can be derived according to eqn (11) or similar equations. The results are summarized in Table 3. The values of $\Delta G_{H^-A}^{\neq}(X^+)$ for the corresponding 187 hydride acceptors (**X**⁺) in acetonitrile at 298 K can be derived from the corresponding $\Delta G_{H^-D}^{\neq}(XH)$ using eqn (6), and the results are also listed in Table 3. In order to conveniently compare $\Delta G_{H^-D}^{\neq}(XH)$ with $\Delta G_{H^-D}^{\circ}(XH)$ and $\Delta G_{H^-A}^{\neq}(X^+)$ with $\Delta G_{H^-A}^{\circ}(X^+)$, the $\Delta G_{H^-D}^{\circ}(XH)$ values of the 187 hydride donors (**XH**) and the $\Delta G_{H^-A}^{\circ}(X^+)$ values of the 187 hydride acceptors (**X**⁺) in acetonitrile at 298 K are also listed in Table 3.

IV. Scales of $\Delta G_{H^-D}^{\neq}(XH)$ and $\Delta G_{H^-A}^{\neq}(X^+)$ of various XH and X⁺ in acetonitrile

From column 2 in Table 3, it is clear that the X-H bond activation energies $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})$ of the 187 organic hydride donors (XH) for hydride self-exchange reactions in acetonitrile range from 39.6 kcal mol⁻¹ for **12H** to 65.8 kcal mol⁻¹ for **52H** (G = p-CF₃). Among the 187 hydride donors, **12H** as the hydride donor is the easiest to be activated, whereas 52H (G = p-CF₃) as the hydride donor is the most difficult to be activated. Such a large scale of the X-H bond activation energies (39.6-65.8 kcal mol⁻¹) indicates that the X-H bond activation energies of hydride donors are strongly dependent on the nature and structure of the hydride donors. For a convenient search of $\Delta G_{\mathrm{H}^-\mathrm{D}}^{\neq}(\mathrm{XH})$ for various types of hydride sources, a simple overview figure is provided (Fig. 5). From column 3 in Table 3, it is clear that the scale of $\Delta G_{H^-A}^{\neq}(X^+)$ for the 187 diverse hydride acceptors (X^{+}) ranges from -1.9 kcal mol⁻¹ for 24^{+} to -37.1 kcal mol⁻¹ for 56⁺. Among the 187 X⁺, 24⁺ is the kinetically weakest hydride acceptor, whereas 56⁺ is the kinetically strongest one. Such a large scale of the X-H bond formation energies of X^+ in the transition states (-1.9 to -37.1 kcal mol^{-1}) indicates that the X-H bond formation energies of X^{+} (*i.e.*, the free energy change of \mathbf{X}^{\dagger} from the initial state to the transition state) is also strongly dependent on the nature and the structure of the hydride acceptors (X^{*}) . For a convenient search of $\Delta G_{H^-A}^{\neq}(X^+)$ for various types of hydride acceptors, a simple overview figure is provided (Fig. 6). If the $\Delta G_{H^-D}^{\neq}(XH)$ values of the 187 **XH** and the $\Delta G_{H^-A}^{\neq}(X^+)$ values of the corresponding 187 X^+ are compared, it is found that the easiest activation of the X-H bond does not indicate the easiest formation of $(X-H)^{\neq}$. That is because the $\Delta G^{\circ}_{H^-D}(XH)$ values of the 187 XH in acetonitrile are different from each other. If $\Delta G_{H^-D}^{\neq}(XH)$ of various hydride donors (XH) are compared with the corresponding $\Delta G^{\circ}_{H^-D}(XH)$, such a relation $1/2\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH}) < \Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH}) < \Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})$ could be observed. Similarly, if the numerical values of $\Delta G_{H^-A}^{\neq}(X^+)$ and

 $\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+}) \ [\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+}) = -\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{X}\mathrm{H})]$ are compared with each other, the former is even smaller than half of the latter. This result indicates that for any organic hydride donor (XH), the numerical value of $\Delta G_{H^-A}^{\neq}(X^+)$ is always smaller than that of the corresponding $\Delta G_{H^-D}^{\neq}(XH)$. Actually, the X–H bond activation energy of XH, $\Delta G_{H^-D}^{\neq}(XH)$, is the resistant force of the hydride transfer and the X-H formation energy of X⁺, $\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathrm{X}^{+})$, is the driving force. According to the character of the Morse-type curve, it is evident that when the hydride transfer takes place from the initial state to the transition state, the instantaneous driving force $[\partial G_{H^-A}^{\neq}(Y^+)/\partial r]$ is always smaller than the instantaneous resistant force $\left[\partial G_{H^-D}^{\neq}(XH)/\partial r\right]$ and the difference gradually becomes small until zero. When the hydride transfer takes place from the transition state to the final state, the instantaneous driving force $[\partial G_{H^-A}^{\neq}(Y^+)/\partial r]$ is always larger than the instantaneous resistant force $\left[\partial G_{H^-D}^{\neq}(XH)/\partial r\right]$ and the difference gradually increases.

V. The factors affecting $\Delta G^{\neq}_{{\sf H}^-{\sf D}}({\sf X}{\sf H})$ and $\Delta G^{\neq}_{{\sf H}^-{\sf A}}({\sf Y}^+)$

By examining the dependence of $\Delta G_{H^-D}^{\neq}(XH)$ on $\Delta G_{H^-D}^{\circ}(XH)$ (Fig. 7), it is found that $\Delta G_{H^-D}^{\neq}(XH)$ increases with an increase of $\Delta G^{\circ}_{H^-D}(XH)$, which implies that the thermodynamic properties $\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})$ should be one main factor to determine the $\Delta G_{H^-D}^{\neq}(XH)$. However, the relationship between $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})$ and $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\circ}(\mathrm{XH})$ is not of a good linearity and many scattered points appear in the diagram, which indicates that $\Delta G^{\circ}_{H^-D}(XH)$ is not the only factor to affect $\Delta G^{\neq}_{H^-D}(XH)$. From the kinetic theoretic model proposed in this work, $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})$ is dependent not only on $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\circ}(\mathrm{XH})$, but also on the distance between the donor and the acceptor $(\Delta r) \left[\Delta r = 2 \times \right]$ $r_{\rm effi}(\rm XH)$, $r_{\rm effi}(\rm XH)$ is the efficient radius of XH molecule]. For hydride cross transfer reactions (XH + $Y^+ \rightarrow X^+ + YH$, $X \neq Y$), the reaction free energy change ΔG° is also an important factor to affect $\Delta G_{H^-D}^{\neq}(XH/Y^+)$. If these effects were examined qualitatively the results were as follows. In general, for hydride self-exchange reactions, when the distance between the hydride donor and the hydride acceptor (Δr) is kept constant, $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})$ is proportional to $\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\circ}(\mathrm{XH})$ (Fig. 8). For instance, some hydride donors in Table 3, such as 2H-6H, 15H-16H, 21H, 23H, 30H-32H, 37H, 38H, 48H-50H, 52H, 53H, etc. gave excellent experimental evidence. Similarly, for hydride self-exchange reactions, when the $\Delta G^{\circ}_{H^-D}(XH)$ is kept constant, the increase of Δr (*i.e.*, the efficient size of **XH**) can result in a larger $\Delta G_{H^-D}^{\neq}(XH)$ (Fig. 9). In addition, for a hydride cross transfer reaction, when the Δr is kept constant, the more negative the ΔG° is, the smaller the $\Delta G_{H^-D}^{\neq}(XH/Y^+)$ is (Fig. 10).

VI. Estimation of the activation energies of various hydride transfer reactions in acetonitrile

The data in Table 3 are very useful. From $\Delta G^{\circ}_{\mathrm{H}^-\mathrm{D}}(\mathrm{XH})$ and $\Delta G^{\circ}_{\mathrm{H}^-\mathrm{A}}(\mathrm{X}^+)$, the thermodynamic driving forces (ΔG°) of the A^2_{187} (34 782) hydride cross-transfer reactions ($\mathbf{XH} + \mathbf{Y}^+ \rightarrow \mathbf{X}^+ + \mathbf{YH}$,

Table 3 The X–H bond activation free energies of the 187 hydride donors (**XH**) $[\Delta G^{\neq}_{H^-D}(XH)]$ and the X–H bond formation free energies of **X**⁺ $[\Delta G^{\neq}_{H^-A}(X^+)]$ in the transition state for the hydride self-exchange reactions in acetonitrile as well as the free energy changes of **XH** releasing a hydride anion $[\Delta G^{\circ}_{H^-D}(XH)]$ and the free energy changes of **X**⁺ capturing a hydride anion $[\Delta G^{\circ}_{H^-A}(X^+)]$ together with the activation energies of the hydride self-exchange reactions $[\Delta G^{\neq}(XH)]$ in acetonitrile

Hydride	donors (XH)	$\Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})^{a}$	$[\Delta G^{ eq}_{\mathrm{H}^-\mathrm{A}}(\mathrm{X}^+)]^b$	$\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})^{c}$	$[\Delta G^{\circ}_{\mathrm{H^{-}D}}(\mathrm{X^{+}})]^{d}$	$\Delta G^{\neq}(\mathrm{XH})^{e}$
1H	R = Me	45.31	-14.19	59.5	-59.5	31.1
	Et	45.18	-14.12	59.3	-59.3	31.1
	ⁱ Pr	45.52	-13.78	59.3	-59.3	31.7
	^t But	48.44	-10.86	59.3	-59.3	37.5
	Bn	45.14	-14.16	59.3	-59.3	30.9
	Ph	46.81	-12.39	59.2	-59.2	34.4
2H	G = p-MeO	42.89	-15.31	58.2	-58.2	27.6
	<i>p</i> -Me	42.98	-15.72	58.7	-58.7	27.3
	p-H	43.04	-16.26	59.3	-59.3	26.7
	p-F	43.07	-16.33	59.4	-59.4	26.8
	p-Cl	43.27	-16.83	60.1	-60.1	26.5
	p-CN	43.68	-17.72	61.4	-61.4	26.0
3H	G = p-MeO	43.69	-17.61	61.3	-61.3	26.1
011	<i>n</i> -Me	43.73	-17.87	61.6	-61.6	25.8
	<i>p</i> -H	43.92	-18.28	62.2	-62.2	25.6
	<i>p</i> 11 <i>p</i> -F	44.00	-18.3	62.3	-62.3	25.0
	p I n-Cl	44.09	-18.61	62.7	-62.7	25.5
	p Cl p-CN	44.05	_10.85	64.1	-64.1	20.0
11	f = n MeO	43.20	-16.61	60.0	-60.0	24.4
411	g = p-MeO	43.35	16.05	60.2	-00.0	20.8
	<i>p</i> -Me	43.43	-10.85	60.0	-60.3	20.0
	р-н	43.37	-17.33	60.9	-60.9	20.3
	<i>p</i> -F	43.71	-17.29	61.0	-61.0	26.4
	p-CI	43.78	-17.92	61.7	-61.7	25.9
	<i>p</i> -CN	44.25	-18.75	63.0	-63.0	25.5
5H	G = p-MeO	45./1	-19.09	64.8	-64.8	26.6
	<i>p</i> -ме	45.76	-19.44	65.2	-65.2	26.4
	<i>р</i> -н	45.91	-19.69	65.6	-65.6	26.2
	p-F	45.99	-19.61	65.6	-65.6	26.4
	<i>p</i> -CN	46.45	-21.25	6/./	-6/./	25.2
6H	G = p-MeO	45.84	-19.46	65.3	-65.3	26.3
	<i>р</i> -ме	45.87	-19.83	65./	-65./	26.1
	<i>р</i> -н	46.07	-20.33	66.4	-66.4	25.8
	p-F	46.36	-20.14	66.5	-66.5	26.3
	p-Cl	46.68	-20.82	67.5	-67.5	25.9
	<i>p</i> -CN	47.02	-21.98	69.0	-69.0	25.0
7H	R = Me	42.25	-13.55	55.8	-55.8	28.7
	Et	42.36	-14.24	56.6	-56.6	28.2
	'Pr	42.86	-13.04	55.9	-55.9	29.9
	"But	42.15	-14.25	56.4	-56.4	28.0
8H		43.68	-18.92	62.6	-62.6	24.8
9H		42.98	-15.92	58.9	-58.9	27.1
10H		43.37	-17.63	61.0	-61.0	25.8
11H		39.77	-8.33	48.1	-48.1	31.5
12H		39.58	-3.52	43.1	-43.1	36.1
13H		42.93	-13.67	56.6	-56.6	29.2
14H		45.31	-17.99	63.3	-63.3	27.3
15H	G = p-MeO	44.12	-17.78	61.9	-61.9	26.3
	<i>p</i> -Me	44.35	-18.25	62.6	-62.6	26.1
	<i>р</i> -Н	44.70	-19.20	63.9	-63.9	25.5
	p-Cl	45.30	-20.00	65.3	-65.3	25.3
	<i>p</i> -Br	45.34	-20.16	65.5	-65.5	25.1
16H	G = p-MeO	44.21	-16.29	60.5	-60.5	27.9
	<i>p</i> -Me	44.54	-16.56	61.1	-61.1	27.9
	p-H	44.84	-17.56	62.4	-62.4	27.2
	p-Cl	45.59	-18.51	64.1	-64.1	27.1
	<i>p</i> -Br	45.59	-18.61	64.2	-64.2	27.0
17H	r =-	42.57	-21.83	64.4	-64.4	20.8
18H		45.14	-19.06	64.2	-64.2	26.0
19H		45.99	-24.91	70.9	-70.9	21.1
20H		44.95	-24.05	69.0	-69.0	20.9

Paper

Hydride do	onors (XH)	$\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})^{a}$	$\left[\Delta G^{ eq}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+}) ight]^{b}$	$\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{X}\mathrm{H})^{c}$	$[\Delta G^{\circ}_{\mathrm{H^{-}D}}(\mathrm{X^{+}})]^{d}$	$\Delta G^{\neq}(\mathrm{XH})^{e}$
21H	$G = p-NMe_2$	41.56	-4.14	45.7	-45.7	37.5
	<i>p</i> -MeO	42.22	-5.78	48.0	-48.0	36.4
	<i>p</i> -Me	42.35	-6.15	48.5	-48.5	36.2
	<i>р</i> -Н	42.54	-6.66	49.2	-49.2	35.8
	<i>p</i> -Cl	43.04	-7.26	50.3	-50.3	35.7
	p-CF ₃	43.38	-8.22	51.6	-51.6	35.2
	<i>p</i> -CN	43.68	-8.12	51.8	-51.8	35.6
	p-NO ₂	43.89	-8.31	52.2	-52.2	35.6
	<i>р</i> -ОН	42.61	-5.09	47.7	-47.7	37.5
	o-OH	42.61	-6.29	48.9	-48.9	36.3
	o-Me	44.43	-2.07	46.5	-46.5	42.3
	o-Cl	42.61	-5.69	48.3	-48.3	36.9
22H		41.47	-3.13	44.6	-44.6	38.4
23H	G = p-MeO	47.53	-5.37	52.9	-52.9	42.1
	<i>p</i> -Me	47.74	-5.46	53.2	-53.2	42.2
	<i>р</i> -Н	47.87	-5.83	53.7	-53.7	42.1
	<i>p</i> -Br	48.28	-6.22	54.5	-54.5	42.1
	p-CF ₃	48.75	-6.75	55.5	-55.5	42.0
24H		46.88	-1.92	48.8	-48.8	45.0
25H		42.92	-9.78	52.7	-52.7	33.1
26H		43.16	-11.14	54.3	-54.3	32.1
27H		53.71	-11.99	65.7	-65.7	41.7
28H		45.21	-24.49	69.7	-69.7	20.7
29H		48.12	-27.58	75.7	-75.7	20.5
30H	G = p-MeO	46.41	-21.89	68.3	-68.3	24.5
	<i>p</i> -Me	46.56	-22.34	68.9	-68.9	24.3
	<i>р</i> -Н	46.81	-23.09	69.9	-69.9	23.7
	<i>p</i> -Br	47.26	-24.04	71.3	-71.3	23.3
	p-Cl	47.22	-23.58	70.8	-70.8	23.6
	<i>m</i> -Cl	47.41	-24.19	71.6	-71.6	23.2
31H	G = p-MeO	46.61	-21.19	67.8	-67.8	25.4
	<i>p</i> -Me	46.67	-22.33	69.0	-69.0	24.4
	<i>p</i> -Br	47.12	-24.78	/1.9	-/1.9	22.3
	p-Cl	47.18	-24.02	/1.2	-/1.2	23.2
	<i>m</i> -Cl	47.37	-25.53	/2.9	-/2.9	21.9
32H	G = p-MeO	46.56	-22.84	69.4	-69.4	23.8
	<i>р</i> -ме	46.72	-22.88	69.6	-69.6	23.8
	<i>p</i> -Br	47.24	-23.26	70.5	-70.5	23.9
	p-CI	47.22	-23.18	70.4	-70.4	24.0
2211	<i>m</i> -CI	47.41	-23.39	70.8	-70.8	24.0
33H		49.17	-23.43	/2.6	-72.6	25.8
34H	$C = \pi M_{\pi} O$	51.48	-18.42	69.9	-69.9	33.1
35H	G = p-MeO	51.97	-21.83	/3.8	-/3.8	30.2
	<i>p</i> -Me	52.04	-22.06	74.1	-74.1	29.9
	p-H	52.07	-20.73	72.8	-72.8	31.4
	p-CI	52.15	-22.45	74.6	-74.6	29.7
2611	$p - nO_2$	52.34	-22.96	/5.3	-75.3	29.3
30H	G = p-MeO	49.92	-13.38	63.3	-63.3	36.5
	<i>p</i> -Me	50.13	-13.57	63.7	-63.7	36.5
	<i>p</i> -п	50.23	-14.07	64.3	-64.3	30.1
	<i>p</i> -CI	50.76	-14.74	65.5	-65.5	30.1
2711	p-CF ₃	51.24	-15.56	60.1	-66.8	35.6
3/H	G = p-MeO	49.61	-12.49	62.1	-62.1	37.1
	<i>p</i> -Me	49.77	-12.83	62.6	-62.6	37.0
	р-н	50.02	-13.18	63.2	-63.2	36.8
	p-CI	50.52	-14.18	64./	-64./	36.3
2017	p-CF ₃	51.09	-14.91	66.0	-66.0	36.2
38H	G = p-MeO	49.67	-10.63	60.3	-60.3	39.1
	<i>p</i> -Me	50.06	-10.74	60.8	-60.8	39.4
	р-н	50.25	-11.45	61.7	-61.7	38.8
	p-Cl	50.80	-12.8	63.6	-63.6	38.0
	p-CF ₃	51.32	-13.98	65.3	-65.3	37.3
39H	R = H	49.98	-15.02	65.0	-65.0	35.0
	Mo	49.74	-12.46	63.2	-63.2	36.2
	IVIC	49.74	-13.40	03.2	-03.2	30.2

Hydride	donors (XH)	$\Delta G_{\mathrm{H}^{-}\mathrm{D}}^{\neq}(\mathrm{XH})^{a}$	$\left[\Delta G^{ eq}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+}) ight]^{b}$	$\Delta G^{\circ}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})^{c}$	$\left[\Delta G^{^{\mathrm{o}}}_{\mathrm{H^{-}D}}(\mathrm{X}^{+}) ight]^{d}$	$\Delta G^{\neq}(XH)^{e}$
40H	G = <i>p</i> -MeO	46.97	-13.73	60.7	-60.7	33.3
	<i>p</i> -Me	47.05	-13.95	61.0	-61.0	33.1
	р-Н	47.11	-14.29	61.4	-61.4	32.8
	<i>p</i> -Cl	47.43	-14.57	62.0	-62.0	32.8
	p-CF ₃	47.70	-15.20	62.9	-62.9	32.5
41H	G = p-MeO	46.93	-13.37	60.3	-60.3	33.5
	<i>p</i> -Ме	47.01	-13.49	60.5	-60.5	33.5
	<i>р</i> -Н	47.08	-13.82	60.9	-60.9	33.3
	<i>p</i> -Cl	47.40	-14.30	61.7	-61.7	33.1
	p-CF ₃	47.67	-14.93	62.6	-62.6	32.8
42H	G = p-MeO	47.06	-12.74	59.8	-59.8	34.4
	<i>p</i> -Ме	47.14	-12.86	60.0	-60.0	34.2
	<i>р</i> -н	47.27	-13.03	60.3	-60.3	34.3
	<i>p</i> -Cl	47.49	-13.61	61.1	-61.1	33.9
	p-CF ₃	47.77	-14.33	62.1	-62.1	33.5
43H	R = H	47.54	-15.86	63.4	-63.4	31.6
	Me	46.17	-11.93	58.1	-58.1	34.3
	Et	46.40	-12.80	59.2	-59.2	33.6
44H	G = p-MeO	44.26	-18.54	62.8	-62.8	25.8
	<i>р</i> -Ме	44.36	-19.34	63.7	-63.7	25.1
	<i>р</i> -н	44.47	-20.03	64.5	-64.5	24.5
4.511	p-F	44.53	-20.47	65.0	-65.0	24.0
45H	G = p-MeO	49.76	-16.64	66.4	-66.4	33.2
	<i>p</i> -ме	49.82	-17.68	67.5	-6/.5	32.1
	p-н л Ol	49.99	-18.11	68.1	-68.1	31.9
	<i>p</i> -CI	50.37	-18.83	69.2	-69.2	31.6
4611	p - CF_3	51.05	-19.85	70.9	-70.9	31.2
4011		48.04	-28.10	/0.2	-76.2	19.8
4/H 4011	$C = n M_0 O$	52.69	-10.51	72.0	-03.2	42.2
40 П	G = p-MeO	47.33	-23.37	72.9	-72.9	22.1
	p-Me	47.97	-25.55	75.5	-75.5	22.3
	p-11 p-Cl	51.88	-25.54	78.2	-78.2	25.7
	p-CI n-CF	54.75	-27.05	91.9		23.0
49H	$p \circ r_3$ G = n-MeO	46.33	-25.37	71 7	-71 7	27.7
1,111	n-Me	47.26	-25.54	72.8	-72.8	20.9
	p Mc n-H	48.53	-25.57	74.1	-74 1	221.0
	p II n-Cl	49.93	-25.87	75.8	-75.8	24.0
	<i>p</i> -CF ₂	52.38	-26.02	78.4	-78.4	26.4
50H	G = n - MeO	60.62	-32.28	92.9	-92.9	28.3
0011	<i>p</i> -Me	60.95	-32.85	93.8	-93.8	28.1
	<i>p</i> -H	61.22	-33.08	94.3	-94.3	28.1
	p-Cl	61.81	-33.39	95.2	-95.2	28.4
	p-CF ₂	63.01	-33.69	96.7	-96.7	29.3
51H	1 5	58.64	-36.96	95.6	-95.6	21.6
52H	G = p-MeO	59.71	-33.79	93.5	-93.5	25.9
	<i>p</i> -Me	60.28	-34.02	94.3	-94.3	26.3
	p-H	61.92	-34.08	96.0	-96.0	27.8
	p-Cl	63.31	-34.29	97.6	-97.6	29.0
	p-CF ₃	65.83	-34.47	100.3	-100.3	31.3
53H	G = p-MeO	56.68	-33.52	90.2	-90.2	23.2
	<i>p</i> -Me	56.93	-33.67	90.6	-90.6	23.2
	р-Н	57.59	-34.01	91.6	-91.6	23.6
	p-Cl	58.16	-34.34	92.5	-92.5	23.9
	<i>p</i> -Br	59.20	-34.3	93.5	-93.5	24.9
	p-CF ₃	57.14	-34.66	91.8	-91.8	22.4
	<i>m</i> -MeO	57.13	-34.17	91.3	-91.3	22.9
	<i>m</i> -Me	59.22	-33.88	93.1	-93.1	25.3
	m-CF ₃	61.03	-34.57	95.6	-95.6	26.4
54H		55.81	-30.39	86.2	-86.2	25.4
55H		48.83	-28.57	77.4	-77.4	20.2
56H		63.57	-37.13	100.7	-100.7	26.5

^{*a*} The values of $\Delta G_{H^-D}^{\neq}(XH)$ were derived from eqn (11) or the corresponding similar equations. The unit is kcal mol⁻¹. The related parameters were all derived from Table 2. ^{*b*} Derived from eqn (6), the unit is kcal mol⁻¹. ^{*c*} Derived from molar free energy changes of the hydride transfer reactions listed in Table 2 and the corresponding free energy changes of the hydride acceptors to capture hydride anions in acetonitrile at 298 K. The unit is kcal mol⁻¹. ^{*d*} $\Delta G_{H^-A}^{\circ}(X^+) = -[\Delta G_{H^-D}^{\circ}(XH)]$. ^{*e*} $\Delta G^{\neq}(XH/X^+) = \Delta G_{H^-D}^{\neq}(XH) + \Delta G_{H^-A}^{\neq}(X^+)$. The unit is kcal mol⁻¹.

Paper



Fig. 5 An overview figure of $\Delta G_{H-D}^{\neq}(XH)$ for various types of hydride donors in acetonitrile at 298 K; the unit is kcal mol⁻¹.

X ≠ **Y**) can be derived from eqn (2). In a similar way, from $\Delta G_{\mathrm{H}^-\mathrm{D}}^{\neq}(\mathrm{XH})$ and $\Delta G_{\mathrm{H}^-\mathrm{A}}^{\neq}(\mathrm{X}^+)$, the activation energies of 187 hydride self-exchange reactions (**XH** + **X**⁺ → **X**⁺ + **XH**) and the A_{187}^{2} (34 782) hydride cross-transfer reactions (**XH** + **Y**⁺ → **X**⁺ + **YH**) can be readily derived from eqn (4), respectively. The results of the 187 hydride self-exchange reactions (**XH** + **X**⁺ → **X**⁺ + **XH**) are listed in Table 3, which ranges from 19.8 kcal mol⁻¹ for **46H** to 45.0 kcal mol⁻¹ for **24H**. Since the activation energies of the hydride self-exchange reactions in acetonitrile are all much greater than the highest limit of 14.7 kcal mol⁻¹ [equivalent to $k_{\text{self}}(\text{XH}/\text{X}^+) = 1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$] that can be directly determined by the dynamic ¹H NMR method, it is not

difficult to understand why the hydride self-exchange reactions cannot be directly determined. In fact, for many hydride donors, such as **23H**, **24H**, **47H**, *etc.*, the hydride self-exchange reactions are too slow to take place. For more than thirty thousand (A_{187}^2) hydride cross transfer reactions (**XH** + **Y**⁺ \rightarrow **X**⁺ + **YH**, X \neq Y), the detailed results of the estimated activation energies were not listed to save space, but a range of data was given here. The result is from 63.9 kcal mol⁻¹ for the hydride transfer from **52H** to **24**⁺ to 2.5 kcal mol⁻¹ for the hydride transfer from **12H** to **56**⁺ in acetonitrile. Evidently, the activation energy of the fastest hydride transfer reaction has surpassed the activation energy limit of the diffusion limited



Fig. 6 An overview figure of $\Delta G_{H^-A}^{\neq}(X^+)$ for various types of hydride acceptors in acetonitrile at 298 K; the unit is kcal mol⁻¹.





Fig. 8 Dependence of the bond activation free energies of organic hydride donors (**XH**) for the hydride self-exchange reactions, $\Delta G_{H^-D}^{\neq}(XH)$, on $\Delta G_{H^-D}^{\circ}(XH)$ when Δr is kept constant.

Fig. 7 Relationship between the X–H bond activation free energies of the 187 organic hydrides (**XH**) for their hydride self-exchange reactions and the corresponding free energy changes of **XH** to release a hydride anion in acetonitrile at 298 K.



Fig. 9 Dependence of the bond activation free energies of organic hydride donors (**XH**) for the hydride self-exchange reactions on the distance between the hydride donor and the hydride acceptor (Δr).



Fig. 10 Dependence of the bond activation free energies of organic hydride donors (**XH**) at the transition state for the hydride cross transfer reactions on the free energy changes of the reactions (ΔG°) when Δr is kept constant.

chemical reactions (in general, $\Delta G^{\neq} < 3.8$ kcal mol⁻¹ (equivalent to $k > 10^{10}$ M⁻¹ s⁻¹) for the diffusion limited reactions;⁵⁴ but it is impossible for the slowest one to take place in the solution at 298 K). As we know, there are many important organic hydride transfer reactions *in vivo* or *in vitro* whose rates cannot be directly measured by using experimental methods up to now. The reason is that some reactions are too fast, some are too slow and some have no detectable signals, *etc.* Evidently, a reliable method is urgently required to estimate the activation energies.

VII. Validity of eqn (4)

In order to verify the validity of the kinetic equation (eqn (4)), which has been used to estimate the activation energies of

more than thirty thousand hydride cross-transfer reactions and 187 hydride self-exchange reactions, the activation energies of hydride transfer from **1H** to **53**⁺ in acetonitrile (eqn (18)) and the activation energies of hydride self-exchange reaction of $AcrH_2$ with the corresponding cation ($AcrH^+$) in acetonitrile (eqn (19)) were determined by independent experimental methods.

The activation energies of hydride transfer reaction from **1H** to **53**⁺ in acetonitrile can be measured by the stopped-flow UV-vis method. The determined results and the corresponding results predicted according to eqn (4) are listed together in Table 4. The perfect agreement between the two results⁵⁵ does indicate not only that the values of $\Delta G_{H^-D}^{\neq}(XH)$ and $\Delta G_{H^-A}^{\neq}(X^+)$ derived from this work are reliable, but also that eqn (4) is valid to predict the activation energies of the hydride cross-transfer reactions.^{35b,56}



As to the hydride self-exchange reaction of AcrH₂ with the corresponding cation (AcrH⁺) (eqn (19)), the activation energy of the reaction in acetonitrile cannot be directly determined by the conventional experimental method, since no spectral signal can be detected to describe the reaction progress. However, the activation energy of hydride transfer from (N-CH₃)AcrH₂ to (N-CD₃)AcrH⁺ in CD₃CN (eqn (20)) can be determined by the conventional ¹H NMR technique, since the chemical shifts of the CH₃-group in AcrH₂ (3.36 ppm) and in AcrH⁺ (4.76 ppm) are different (Fig. 11) and the kinetic isotope effect of deuterium in the CD₃ group on the hydride transfer reaction should be quite small (due to the secondary kinetic isotope effect). The perfect agreement between the experimental result (19.7 kcal mol^{-1}) and the theoretical figure (19.8 kcal mol^{-1}) does indicate that eqn (4) is also valid to predict the activation energies of the hydride self-exchange reactions.

Table 4	Experimental and theoretica	rate constants of hydride	cross transfer reactions from	1H to 53 ⁺ in acetonitrile at 298 K
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Hydride donors (1H)	Hydride acceptors	$\Delta G^{ eq}_{\mathrm{H^{-}D}}(\mathbf{1H})^{a}$	$\Delta G^{ eq}_{\mathrm{H^-A}}(\mathbf{53^+})^b$	$\Delta G^{\neq}(ext{calc.})^c$	$\Delta G^{\neq}(\exp.)^d$
R = H	53 ⁺	43.04	-33.52	9.5	9.4
Ме	53^{+}	45.31	-33.52	11.8	12.0
Et	53^{+}	45.18	-33.52	11.7	11.5
ⁱ Pr	53^{+}	45.52	-33.52	12.0	11.9
ⁿ But	53^{+}	48.44	-33.52	14.9	15.1
Bn	53^{+}	45.14	-33.52	11.6	11.5
Ph	53^{+}	46.81	-33.52	13.3	13.1

^{*a*} From column 2 in Table 3, the unit is kcal mol⁻¹. The uncertainty is smaller than 0.5 kcal mol⁻¹. ^{*b*} From column 3 in Table 3, the unit is kcal mol⁻¹. ^{*c*} Derived from eqn (4), the unit is kcal mol⁻¹. ^{*d*} Obtained from the experimental measurements by using the UV-vis method; the unit is kcal mol⁻¹. The uncertainty is smaller than 0.1 kcal mol⁻¹.



Fig. 11 ¹H NMR spectra changes of the mixture of $(N-CH_3)AcrH_2$ (0.0253 mol L⁻¹) and $(N-CD_3)AcrH^+$ (0.0126 mol L⁻¹) in CD₃CN at 298 K. From top to bottom, the reaction times are 23 min, 70 min, 118 min, 260 min and 354 min, respectively.



VIII. Summary and conclusions

(1) In this work, a classical but new kinetic equation $\Delta G^{\neq} = \Delta G_{H^-D}^{\neq}(XH) + \Delta G_{H^-A}^{\neq}(Y^+)$ was developed using the Morse-type free energy curves of hydride donors (**XH**) to release a hydride ion and hydride acceptors (**Y**⁺) to capture a hydride ion according to transition state theory, which can be used to estimate the activation energies of various hydride transfer reactions.

(2) The bond activation free energy of hydride donors (**XH**) for the hydride self-exchange reaction $[\Delta G_{H^-D}^{\neq}(XH)]$ as a new physical concept was defined in this work, which can be used to scale the resistant force of the hydride donors (**XH**) to release a hydride ion in kinetics.

(3) The bond formation free energy of hydride acceptors (\mathbf{Y}^{\dagger}) in the transition state for the hydride self-exchange reaction $[\Delta G_{\mathrm{H}^{-}\mathrm{A}}^{\neq}(\mathbf{Y}^{+})]$ as a new physical concept was defined in this work, which can be used to scale the driving force of the hydride acceptors (\mathbf{Y}^{\dagger}) to capture a hydride ion in kinetics.

(4) The magnitude of $\Delta G_{H^-D}^{\neq}(XH)$ of hydride donors (**XH**) is dependent not only on the strength of the X–H chemical bond $[\Delta G_{H^-D}^{\circ}(XH)]$, but also on the effective radius of **XH**. In general, the larger the $\Delta G_{H^-D}^{\circ}(XH)$ is and/or the larger the effective radius of **XH** is, the larger the $\Delta G_{H^-D}^{\neq}(XH)$ is. The magnitude of $\Delta G_{H^-A}^{\neq}(Y^+)$ of hydride acceptors (Y^+) is dependent not only on the hydride affinity of Y^+ [$\Delta G_{H^-A}^{\circ}(Y^+)$], but also on the effective radius of Y^+ . In general, the larger the $\Delta G_{H^-A}^{\circ}(Y^+)$ is and/or the smaller the effective radius of Y^+ is, the larger the $\Delta G_{H^-A}^{\neq}(Y^+)$ is.

(5) An efficient method was developed to determine $\Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})$ of hydride donors and $\Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{Y}^{+})$ of hydride acceptors and the values of $\Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{D}}(\mathrm{XH})$ for 187 typical hydride donors in acetonitrile and the values of $\Delta G^{\neq}_{\mathrm{H}^{-}\mathrm{A}}(\mathrm{X}^{+})$ for 187 typical hydride acceptors (\mathbf{X}^{+}) in acetonitrile were determined.

(6) The activation energies of 187 typical hydride selfexchange reactions and more than thirty thousand (A_{187}^2) hydride cross transfer reactions in acetonitrile at 298 K were estimated.

(7) Since the development of the kinetic equation is only on the basis of the changes of chemical bond of reactants, the kinetic equation should be also suitable for proton transfer reactions, hydrogen atom transfer reactions and all the other chemical reactions involved with breaking and formation of chemical bonds.

Due to the same formats of eqn (2) and (4), one of the most significant contributions of this work is to have achieved the perfect unity between the kinetic equation and thermodynamic equation for hydride transfer reactions.

IX. Experimental section

Materials

All reagents were of commercial quality from freshly opened containers or were purified before use. The reagent grade acetonitrile was refluxed over KMnO₄ and K₂CO₃ for several hours and was doubly distilled over P_2O_5 under argon before use. The 187 organic hydride compounds (**XH**) and their corresponding salts perchlorate (X⁺ClO₄⁻) were synthesized according to conventional synthetic strategies,⁵⁷ or directly according to a literature method.⁵⁸ All the target products were identified by ¹H NMR and MS.

Isothermal titration calorimetry (ITC)

The titration experiments were performed on a CSC4200 isothermal titration calorimeter in acetonitrile at 298 K as described previously.³⁵⁻³⁹ The performance of the calorimeter was checked by measuring the standard heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution. Data points were collected every 2 s. The heat of reaction was determined by following 10 automatic injections from a 250 µL injection syringe containing a standard solution (2 mM) into the reaction cell (1.30 mL) containing 1 mL of the other concentrated reactant (~10 mM). Injection volumes (10 μ L) were delivered in 0.5 s time intervals with 300-450 s between every two injections. The reaction heat was obtained by integration of each peak except the first. Note: typically the first injection shows less heat than expected. This is often due to diffusion across the tip of the needle or to difficulties in positioning the burette drive.

Kinetic measurements

The kinetics of the hydride transfer reactions were conveniently monitored using an Applied Photophysics SX.18MV-R stopped-flow which was thermostated at 298 to 318 K under strictly anaerobic conditions in dry acetonitrile.⁵⁹ The method of kinetic measurement was a pseudo-first-order method. The concentration of the hydride donor was maintained at more than 20-fold excess of the hydride acceptor to attain pseudo-first-order conditions. The kinetic traces were recorded using an Acorn computer and analysed by Pro-K Global analysis/simulation software or translated to PC for further analysis. The data fitting used the equation Abs = $P1 \times EXP(-P2 \times x) + P3$, which was integrated using the Pro-K Global analysis/simulation software or Origin Software, and P2 was the pseudo-first-order rate constant k_1 . Thus the secondorder observed rate constant (k_{obs}) was derived from plots of the pseudo-first-order rate constants versus the concentrations of the excess reactants. In each case, it was confirmed that the rate constants derived from three to five independent measurements agreed within an experimental error of $\pm 5\%$.

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