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Supporting Information

A Classical but New Kinetic Equation for Hydride Transfer Reactions

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Examination of Entropy Change of Hydride Transfer Reaction with the Type of XH + Y^+ → X^+ + YH in Acetonitrile (46H + 55^+ → 46^+ + 55H as an Example)

S1. Determination of Gibbs Free Energy Change of Hydride Transfer from 46H to 55^+ in Acetonitrile

Equal molar **46H** to $\mathbf{55}^+$ were mixed in NMR tube containing CD_3CN and then was incubated at 25 °C. The reaction progress was monitored by ^{1}H NMR technique. The results showed that after ca 10 hours for reaction, the reactions reached the equilibrium state. The equilibrium constant K was derived from the area of peaks at δ = 9.884 ppm for $\mathbf{55}^+$ and the area of peaks at δ = 9.749 ppm for $\mathbf{46}^+$. The result is that K = 7.07 at 25 °C, i.e., Gibbs free energy change $\Delta G^{o}_{(\mathbf{46H/55}^+)}$ = -1.16 kcal/mol. (see Figures S1-S2).

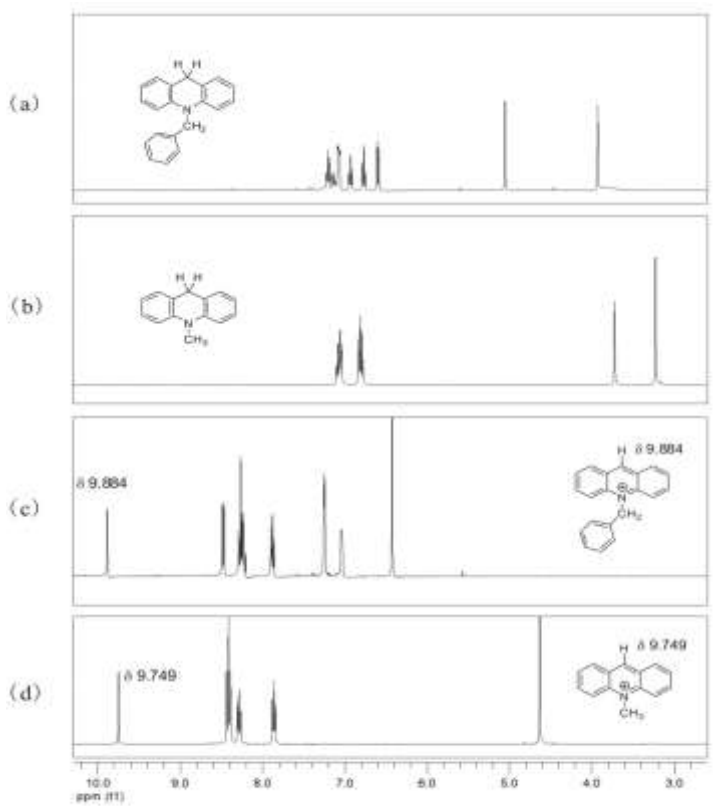

Figure S1 The ^{1}H NMR spectra of **55H** (a), **46H** (b), $\mathbf{55}^+$ (c), $\mathbf{46}^+$ (d) in CD_3CN.

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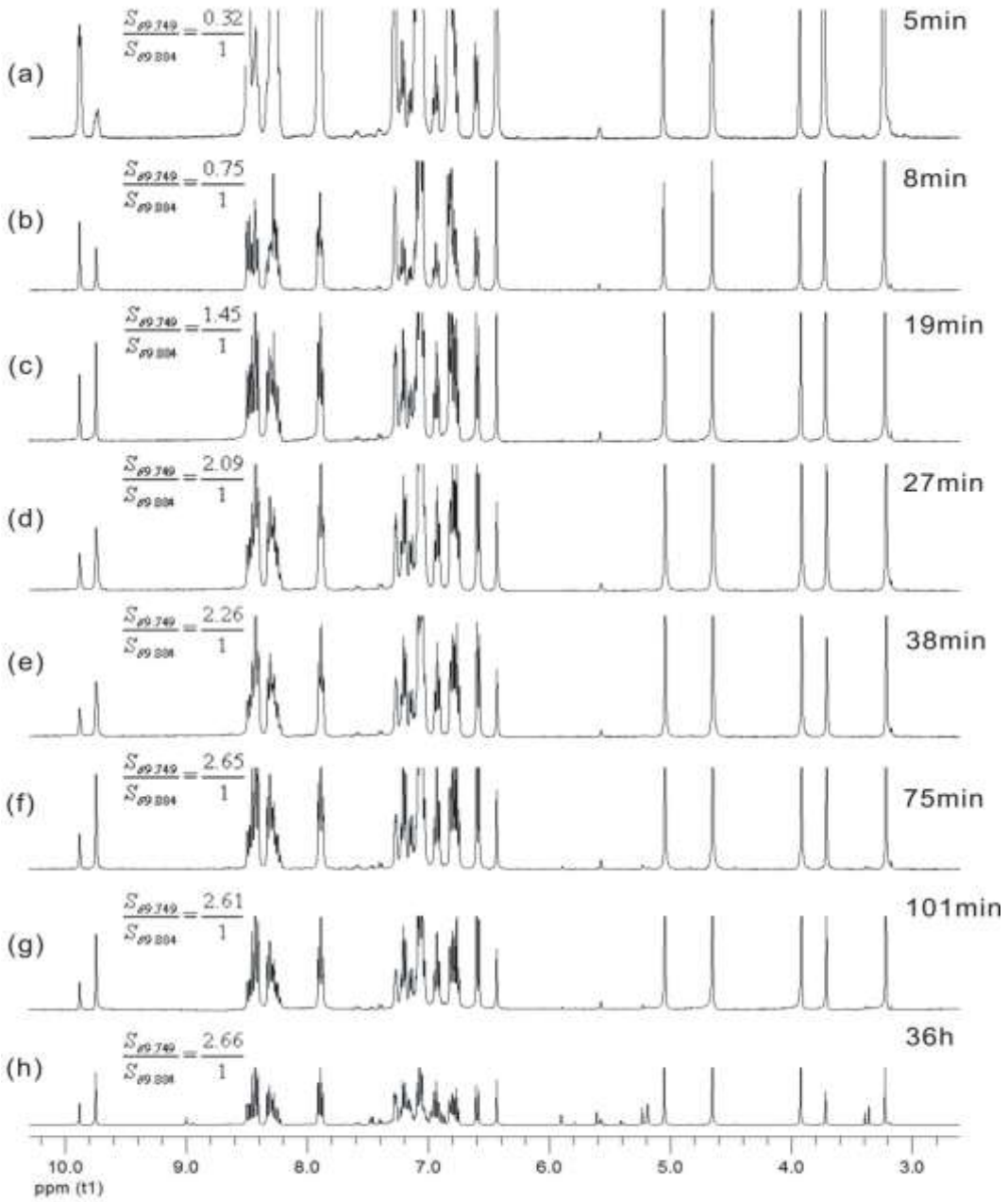

Figure S2 Change in the ^{1}H NMR spectra for the hydride transfer from **46H** to **55**$^+$ to form **46**$^+$ and **55H** in CD_3CN at 298 K with the reaction time. Conditions: the initial molar concentration ratio of **46H** and **55**$^+$ is 1/1: (a) 5 min late; (b) 8 min late; (c) 19 min late; (d) 27 min late; (e) 38 min late; (f) 75 min late; (g) 101 min late; (h) 36 h late.

S2 Determination of Enthalpy Change of Hydride Transfer from 46H to 55$^+$ in Acetonitrile

$\Delta H_{(\mathbf{46H/55}^+)}$ was obtained from the reaction heats of BNAH and **46**$^+$ in acetonitrile (16.9 kcal/mol) and the reaction heat of BNAH with **55**$^+$ in acetonitrile (18.1 kcal/mol), the two reaction heats all were determined in this work. The result is that $\Delta H^o_{(\mathbf{46H/55}^+)}$ = -1.2 kcal/mol. Comparing $\Delta H^o_{(\mathbf{46H/55}^+)}$ and $\Delta G^o_{(\mathbf{46H/55}^+)}$ clear shows that the value of $\Delta H^o_{(\mathbf{46H/55}^+)}$ is quite close to that of $\Delta G^o_{(\mathbf{46H/55}^+)}$, and the

difference is smaller than the experimental error, which means that for the hydride transfer from **46H** to $\mathbf{55}^+$ in acetonitrile, the entropy change, $\Delta S_{(\mathbf{46H}/\mathbf{55}^+)}$, may be ignored. In addition, the dependence of $\Delta G^o_{(\mathbf{46H}/\mathbf{55}^+)}$ on the reaction temperature was examined (Figure S3), the result showed that $\Delta G^o_{(\mathbf{46H}/\mathbf{55}^+)}$ was not dependent on the reaction temperature change, which also supports the suggestion that for the hydride transfer reactions with the type of $\mathbf{XH} + \mathbf{Y}^+ \rightarrow \mathbf{X}^+ + \mathbf{YH}$, $\Delta S^o_{(\mathrm{XH}/\mathrm{Y}^+)}$ of the reactions may be ignored.

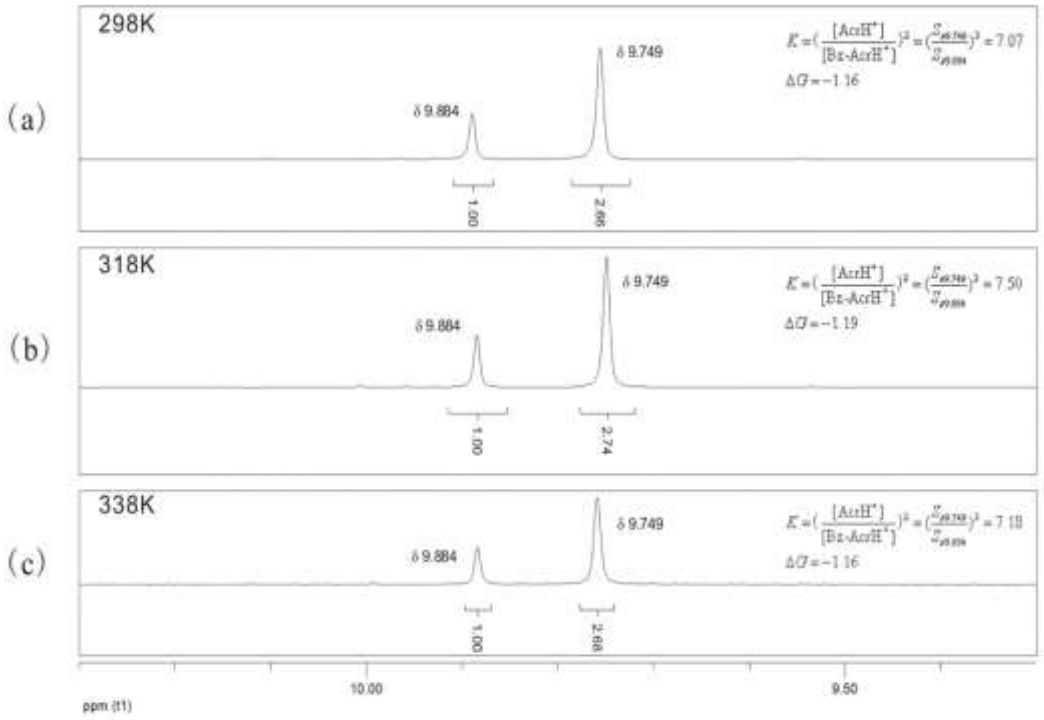

Figure S3 The ^{1}H NMR spectra of the equal molar mixture of **46H** and $\mathbf{55}^+$ in CD_3CN at 298, 318, and 338 K, which was recorded after the reaction reached the equilibrium state.