Supporting Information

A Classical but New Kinetic Equation for Hydride Transfer Reactions

Xiao-Qing Zhu,* Fei-Huang Deng,† Jin-Dong Yang,† Xiu-Tao Li, Qiang Chen, Nan-Ping Lei, Fan-Kun Meng, Xiao-Peng Zhao, Su-Hui Han, Er-Jun Hao, and Yuan-Yuan Mu

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

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

Equal molar \( 46H \) to \( 55^+ \) were mixed in NMR tube containing CD\(_3\)CN 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 \( \delta = 9.884 \) ppm for \( 55^+ \) and the area of peaks at \( \delta = 9.749 \) ppm for \( 46^+ \). The result is that \( K = 7.07 \) at 25 °C, i.e., Gibbs free energy change \( \Delta G^o(46H/55^+) = -1.16 \) kcal/mol. (see Figures S1-S2).

![Figure S1](image)

Figure S1 The \(^1\)H NMR spectra of 55H (a), 46H (b), 55+ (c), 46+ (d) in CD\(_3\)CN.
Figure S2  Change in the $^1$H NMR spectra for the hydride transfer from 46H to 55$^+$ to form 46$^+$ and 55H in CD$_3$CN 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

$\Delta H_{(46H/55^+)}$ 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 $\Delta H_{(46H/55^+)} = -1.2$ kcal/mol. Comparing $\Delta H_{(46H/55^+)}$ and $\Delta G_{(46H/55^+)}$ clear shows that the value of $\Delta H_{(46H/55^+)}$ is quite close to that of $\Delta G_{(46H/55^+)}$.
difference is smaller than the experimental error, which means that for the hydride transfer from $^{46}H$ to $^{55}^+$ in acetonitrile, the entropy change, $\Delta S_{^{46}H/^{55}^+}$, may be ignored. In addition, the dependence of $\Delta G^{\circ}_{\text{reac}}$ on the reaction temperature was examined (Figure S3), the result showed that $\Delta G^{\circ}_{\text{reac}}$ was not dependent on the reaction temperature change, which also supports the suggestion that for the hydride transfer reactions with the type of $\text{XH} + \text{Y}^+ \rightarrow \text{X}^+ + \text{YH}$, $\Delta S^{\circ}_{\text{XHY}^+}$ of the reactions may be ignored.

Figure S3 The $^1H$ NMR spectra of the equal molar mixture of $^{46}H$ and $^{55}^+$ in CD$_3$CN at 298, 318, and 338 K, which was recorded after the reaction reached the equilibrium state.