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Unusual Reaction Constant for Hydride Transfer from a Carbanion to 9-Arylxanthyliums

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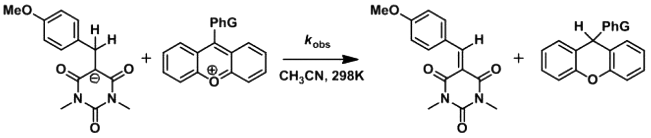
The reaction constant (ρ) from the kinetics for hydride transfer from a carbanion (XH^-) to 9-arylxanthylium ions (9-$GPhXn^+$) in CH_3CN was unusually negative. Thermodynamic analysis indicated that ρ for the simple hydride transfers (only involved with release and capture of a hydride anion) should be positive; this is in contrast to the kinetics results. Consequently, this reaction is not a simple hydride transfer. An "intermediate" was also found in the reaction system, the formation of which resulted in the unusual ρ.

Introduction

Hydride transfer is one of the most fundamental chemical processes.[1] Research on the fundamental scientific problems of hydride-transfer reactions has become a very important field of organic chemistry. For many important organic hydride-transfer reactions in CH_3CN, thermodynamic problems have received good solutions,[2] because for many of the most important organic hydride donors and many typical organic hydride acceptors, such as olefins, imines, quinones, carbonyl compounds, and various organic cations, the free-energy changes associated with the release of hydride anions and the capture of hydride anions in CH_3CN are available.[2–11] For kinetic problems, a classical but new kinetic equation to estimate activation energies of many hydride-transfer reactions has also been developed.[12] Thermodynamic analysis to elucidate the mechanism has been successfully applied in reaction systems such as caffeine,[6] vitamin C[4], and carbanions.[7] Kinetics for mechanistic studies have thus become more important.[4,6,13] The side-equilibrium mechanism of the hydride-transfer reaction from isopropyl alcohol (*i*PrOH) to 9-phenylxanthylium ion ($PhXn^+$, with the adduct *i*PrOPhXn as a side product) has also been determined.[14] Furthermore, model data, as a new method, also reasonably confirmed the charge-transfer (CT) complex.[5] Note that for hundreds of simple hydride transfers (only involved with the release and capture of a hydride anion), the reaction constant (ρ) should be positive, owing to negative charge transfer to the hydride acceptor in the rate-determining step,[7,12] which could be also rationalized by the Hammett equation. Recently, we discovered an inverse result: a negative ρ. To the best of our knowledge, this is the first case in which a hydride-transfer reaction has an unusual reaction constant. In this paper, we wish to report this interesting hydride transfer (Scheme 1).



Scheme 1.

Results and Discussion

The observed reaction rate constants of hydride-transfer reactions in CH_3CN (Scheme 1), the hydride affinities (ΔH_{H^-A}, defined as the molar enthalpy change in X and 9-$GPhXn^+$ to capture a hydride ion in acetonitrile)[8] of X and 9-$GPhXn^+$, the standard one-electron oxidation potentials, and the standard one-electron reduction potentials of the corresponding species were determined. Detailed results are summarized in Tables 1, 2, and 3; see also Scheme 2.

Table 1. Observed rate constants of hydride-transfer reactions from XH^- to 9-$GPhXn^+$ in CH_3CN (Scheme 1).

G	σ	k_{obs}[a] [$\times 10^3$ s^{-1}]
p-CH_3O	–0.27	20.0
p-CH_3	–0.17	11.3
p-H	0	7.2
m-CH_3O	0.12	5.1
p-Cl	0.23	3.2
p-CF_3	0.54	1.2

[a] The experimental error was within 5%; from appearance of the absorbance as a result of the hydride-transfer product.

From Table 1, upon plotting the logarithmic values of k_{obs} against Hammett substituent parameters σ in Figure 1,

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Table 2. Hydride affinities $\Delta H_{\mathrm{H^-A}}$ of X and 9-GPhXn$^+$ in CH_3CN.

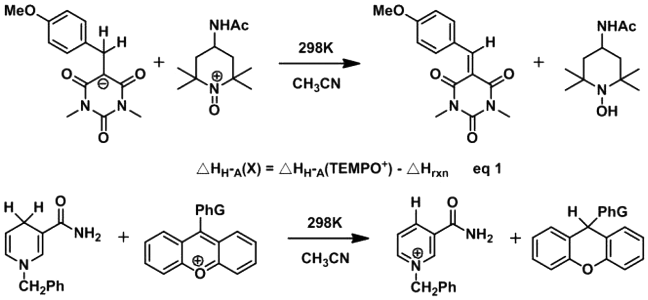
	$\Delta H_{\mathrm{rxn}}(1)$[a] [kcal mol^{-1}]	$\Delta H_{\mathrm{H^-A}}$[b] [kcal mol^{-1}]	$\Delta H_{\mathrm{rxn}}(2)$[a] [kcal mol^{-1}]	$\Delta H_{\mathrm{H^-A}}$[b] [kcal mol^{-1}]
X	–43.4	–62.2		
9-GPhXn$^+$				
p-CH_3O			–30.9	–95.1
p-CH_3			–31.3	–95.5
p-H			–32.3	–96.5
m-CH_3O			–32.5	–96.7
p-Cl			–33.2	–97.4
p-CF_3			–34.2	–98.4

[a] Obtained from the reaction heats by switching the sign. [b] $\Delta H_{\mathrm{H^-A}}$ values were estimated from Eq. (1) and (2) in Scheme 2 by taking $\Delta H_{\mathrm{H-A}}(\mathrm{BNA^+}) = -64.2$ kcal mol^{-1} and $\Delta H_{\mathrm{H^-A}}(\mathrm{TEMPO^+}) = -105.6$ kcal mol^{-1}.[5]

Table 3. Redox potentials of the related species in CH_3CN.

Species (ZH)	$E_{\mathrm{ox}}(\mathrm{ZH})$[a] [mV] CV[b]	$E_{\mathrm{ox}}(\mathrm{ZH})$[a] [mV] OSWV[c]	$E_{\mathrm{red}}(\mathrm{Z^+})$[a] [mV] CV[b]	$E_{\mathrm{red}}(\mathrm{Z^+})$[a] [mV] OSWV[c]
9-GPhXnH				
p-CH_3O	1.167	1.151	–0.436	–0.444
p-CH_3	1.180	1.159	–0.418	–0.420
p-H	1.192	1.173	–0.394	–0.400
m-CH_3O	1.199	1.179	–0.385	–0.390
p-Cl	1.212	1.186	–0.363	–0.368
p-CF_3	1.240	1.207	–0.331	–0.332
XH^-	–0.230	–0.261	–1.510	–1.481

[a] Reproducible to 5 mV or better. [b] CV = cyclic voltammetry. [c] OSWV = Osteryoung square-wave voltammetry.



Scheme 2. TEMPO$^+$ = 4-acetamido-2,2,6,6-tetramethyl-1-oxo-piperidin-1-ium; BNA$^+$ = 1-benzyl-3-carbamoylpyridin-1-ium.

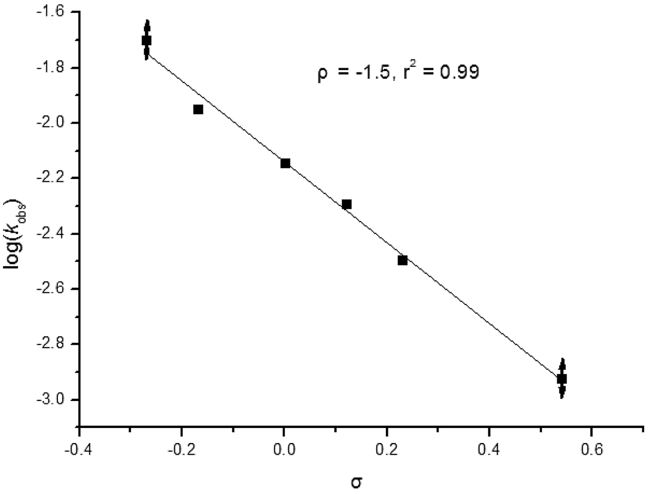
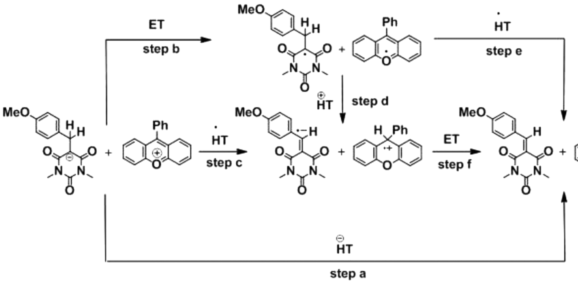


Figure 1. Plot of log(k_{obs}) against the Hammett substituent parameters σ.



Scheme 3.

Table 4. Energies of each reaction step of the hydride transfers from XH^- to 9-GPhXn$^+$ shown in Scheme 3.[a]

	ΔH (or ΔG) [kcal mol^{-1}]					
	step a	step b	step c	step d	step e	step f
p-CH_3O	–32.9	4.2	27.9	23.7	–37.1	–60.8
p-CH_3	–33.3	3.7	27.7	24.0	–37.0	–61.0
p-H	–34.3	3.2	27.1	23.8	–37.5	–61.3
m-CH_3O	–34.5	3.0	26.9	23.9	–37.5	–61.4
p-Cl	–35.2	2.5	26.4	23.9	–37.7	–61.6
p-CF_3	–36.2	1.6	25.9	24.3	–37.8	–62.1

[a] The state energy changes were scaled by using enthalpy changes for steps c–e and by using free energy changes for steps b and f.

the linearity of the six points was very good ($r^2 = 0.99$). Moreover, ρ was negative ($\rho = -1.5$), which was different from previous results. To elucidate the rate-determining step of the simple hydride-transfer reactions from XH- to 9-GPhXn$^+$, thermodynamic analysis for all possible steps was first undertaken (Scheme 3). Thus, the standard energy changes for each reaction step (Table 4) were obtained from Equations (3)–(8).[15]

$$\Delta H(\text{step a}) = \Delta H_{\mathrm{rxn}} = \Delta H_{\mathrm{H^-A\,(X)}} - \Delta H_{\mathrm{H^-A\,(9\text{-}GPhXn^+)}} \quad (3)$$

$$\Delta G(\text{step b}) = -F[E_{\mathrm{red}}(\text{9-GPhXn}^+) - E_{\mathrm{ox}}(\mathrm{XH})] \quad (4)$$

$$\Delta H(\text{step c}) = \Delta H_{\mathrm{rxn}} - F[E_{\mathrm{red}}(\mathrm{X}) - E_{\mathrm{ox}}(\text{9-GPhXnH})] \quad (5)$$

$$\Delta H(\text{step d}) = \Delta H_{\mathrm{rxn}} - F[E_{\mathrm{red}}(\mathrm{X}) - E_{\mathrm{ox}}(\text{9-GPhXnH})] + F[E_{\mathrm{red}}(\text{9-GPhXn}^+) - E_{\mathrm{ox}}(\mathrm{XH})] \quad (6)$$

$$\Delta H(\text{step e}) = \Delta H_{\mathrm{rxn}} + F[E_{\mathrm{red}}(\text{9-GPhXn}^+) - E_{\mathrm{ox}}(\mathrm{XH})] \quad (7)$$

$$\Delta G(\text{step f}) = F[E_{\mathrm{red}}(\mathrm{X}) - E_{\mathrm{ox}}(\text{9-GPhXnH})] \quad (8)$$

Clearly, the process of hydrogen atom transfer (step c) as the first step should be impossible because of the large positive value of the state energy change: 25.9–27.9 kcal mol^{-1} (Table 4), which is greater than 23.1 kcal mol^{-1}.

Because the state energy change of step a is a large negative value (–32.9 to –36.2 kcal mol^{-1}) and that of step b is a positive value (1.6–4.2 kcal mol^{-1}), it seems that the one-step hydride transfer (step a) should be the most likely process. However, Cheng[15] suggested that a multistep mechanism (e$^-$–H$^\cdot$ or e$^-$–H$^+$–e$^-$) would be followed if the energy gap of the initial electron transfer [$\Delta G(\mathrm{e^-_T})$] is considerably smaller than the empirical critical limit of 23.1 kcal mol^{-1} for an endothermic e$^-_\mathrm{T}$, and a one-step hydride transfer may take place if $\Delta G(\mathrm{e^-_T})$ is much greater than 23.1 kcal mol^{-1}. This has been confirmed by several experiments.[7,16] Thus, the possible step is mainly the result of the energy of the initial electron transfer rather than that of the overall hydride transfer, which has also been verified and is accepted by most chemists.[17] So, the only possible initial step for the overall hydride transfer should be electron transfer.

The large positive value of the state energy change (23.7–24.3 kcal mol^{-1}) for proton transfer (step d) and the large negative value (–37.1 to –37.8 kcal mol^{-1}) for that of step e indicates that the only possible second step should be hydrogen atom transfer (step e).

On the basis of the above, the only possible reaction route for simple hydride transfer from XH$^-$ to 9-GPhXn$^+$ should be electron transfer (ET) followed by hydrogen atom transfer; ET should be the rate-determining step. Consequently, the charge transferred to the acceptor in the rate-determining step of the simple hydride transfer from XH$^-$ to 9-GPhXn$^+$ is still a negative charge. According to the Hammett equation, this reaction constant ρ should be positive. Thus, if the reaction was a simple hydride transfer, ρ would be positive. Unfortunately, this contrasts the kinetic results.

The sign of ρ from the kinetic experiment was opposite to that from the thermodynamic analysis for simple hydride transfer, which indicates that this reaction should not be a simple hydride transfer. This was also confirmed by an experiment in which the time required for the formation of hydride transfer product X was longer than 1000 s (Figure 2), whereas the time required for consumption of the reactants (9-GPhXn$^+$) was so fast that it could not be determined with the apparatus.

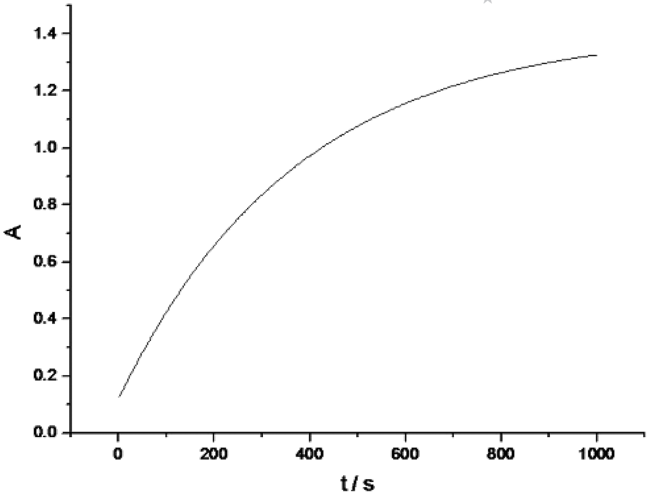
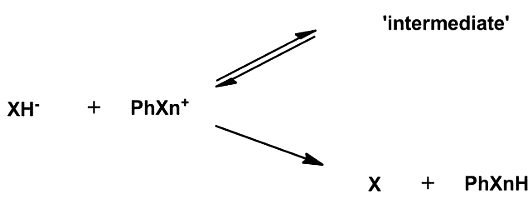


Figure 2. Time-resolved spectrum at 370 nm corresponding to the hydride transfer product X for the reaction of XH$^-$ with 9-ClPhXn$^+$.

Because the time for the formation of the product is much longer than that for the consumption of the reactant, it is reasonable that there was an "intermediate" involved in the hydride-transfer reaction (Scheme 4). The "intermediate" with quotation mark implies that the species involved in the reactions could also be in a side equilibrium[14] with the XH$^-$ and 9-GPhXn$^+$ reactants (Scheme 5). According to the existing literature,[5,14,18] such a possible "intermediate" during hydride transfer may have been the CT complex[5,18] or the adduct.[14] However, we did not find an absorption in the long-wave field region during the reaction that was characteristic of the CT complex.[17,18] This indicated that the formation of the CT complex in this reaction was not possible. Considering the reactivity of the adduct formed between 9-GPhXn$^+$ and XH$^-$, the possible intermediate formed during the reaction was the 9-GPhXnXH adduct. Clearly, this reaction was not a simple hydride transfer as a result of the formation of this "intermediate" in the reaction system, which resulted in the unusual ρ.

$$\mathrm{XH^- + PhXn^+ \rightleftharpoons intermediate \longrightarrow X + PhXnH}$$

Scheme 4.



Scheme 5.

Conclusions

In summary, hydride transfer from XH$^-$ to 9-GPhXn$^+$ was studied. The observed reaction rate constants and the thermodynamic parameters of the corresponding species were determined. We found that the reaction constant ρ from the kinetics was unusually negative, which contrasted the thermodynamic analysis results for simple hydride transfer. Consequently, this reaction is not a simple hydride transfer. Kinetics also confirmed this point: an "intermediate" was formed in the reaction system, which resulted in the unusual ρ. It remains unclear as to whether the "intermediate" is on the way to form GPhXnH or is in a side equilibrium with the reactants. Further mechanistic studies, including characterization of the chemical structure of the "intermediate" described in this work, are currently in progress in this laboratory. We believe that this is a meaningful and new scientific problem that should be researched for hydride-transfer reactions.

Experimental Section

General: All operations were carried in the at 298 K under strict anaerobic conditions in dry CH_3CN. The kinetics of the hydride transfer reactions were conveniently monitored with an Applied Photophysics SX.18MV-R stopped-flow and under first order conditions with the concentration of the hydride donor in at least ten fold excess of that of the hydride acceptor. The rates for the formation of the product were determined from appearance of the absorbance due to the hydride transfer product (X) at λ = 370 nm. The rates for the consumption of the reactants were determined from disappearance of the absorbance due to the hydride transfer reactants (9-GPhXn$^+$) (Herein, for G = p-CH_3O, λ = 497 nm; for G = p-H, λ = 449 nm, and so on). The titration experiments were performed on a CSC4200 isothermal titration calorimeter. The electrochemical experiments were carried out by cyclic voltammetry (CV) and Osteryoung square-wave voltammetry (OSWV) using a BAS-100B electrochemical apparatus.

Supporting Information (see footnote on the first page of this article): Materials and methods, ^{1}H NMR and MS data of typical compounds and measurement of the redox potentials, isothermal titration calorimetry, kinetic measurements, and three thermodynamic cycles.

Acknowledgments

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[15] a) Equations (7) and (8) were derived from three thermodynamic cycles on the basis of Hess' law; see the Supporting Information; b) notably, we used the term free energy change ΔG_{eT} to replace the enthalpy change ΔH_{eT} for the electron-transfer processes. The validation of using the free energy change ΔG_{eT} instead of the enthalpy change ΔH_{eT} for electron-transfer processes is that entropies associated with electron transfer are negligible and ΔG_{eT} can be combined directly with ΔH_{eT}, which was verified by Arnett's work, see: E. M. Arnett, K. Amarnath, N. G. Harvey, J. P. Cheng, *J. Am. Chem. Soc.* **1990**, *112*, 344–355.

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