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Mechanism of Hydride Transfer Reaction from β-Substituted Carbanions to a Carbocation

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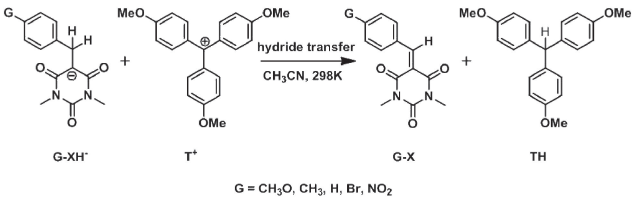
Mechanism of hydride transfer reactions to form olefins is still a conundrum. Here, we propose an electron transfer (ET) followed by hydrogen atom transfer (HT) as the most likely mechanism for hydride transfer reactions from the hydride adducts of olefins (G-XH$^-$) to a carbocation (T$^+$) in acetonitrile. This is confirmed by the analysis of the energetics of each mechanistic step, estimated from $\Delta H_H{}^-$ (the hydride affinity) and redox potentials of the related species, and activation energetics calculated from rate constants of the hydride transfer from G-XH$^-$ to T$^+$.

Olefin is a very important organic unsaturated compound,[1] especially polar olefins.[2–9] Olefins can be reduced by hydride donors such as NADH, $NaBH_4$, and $LiAlH_4$. Because the hydride anion can be split into two electrons and one hydrogen atomic nucleus (or proton), these hydride transfer reactions exhibit a variety of possible mechanisms. The achievements of the related study focused on two aspects: (1) Thermodynamics. This aspect is mainly concerned with the examining of thermodynamic parameters (hydride affinity, hydrogen atom affinity, and so on) of typical compounds such as olefins,[10] aldehydes, ketones,[11] and imines[12] in CH_3CN. (2) Kinetics. On the basis of thermodynamics, a classical but new kinetic equation to estimate activation energies has been developed.[13] Furthermore, using the thermodynamic analysis combining the kinetics to elucidate the hydride transfer reaction mechanism has been successfully applied in the systems of caffeine[14] and vitamin C,[15] which are bioactive. However, the hydride transfer reaction mechanism of carbanions to form olefins has not been studied yet. This is mainly because the kinetic data for the simple hydride transfer are not available, affected by the adduction[16] between the carbanion and the hydride acceptor. Through our tireless efforts, we found the proper acceptor and successfully examined the kinetics of the simple hydride transfer. Here, we report the hydride transfer reaction mechanism of carbanions to form olefins (Scheme 1) using the thermodynamic analysis combining the kinetics.

The substituted 5-benzyl-1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-ide (G-XH$^-$) and tris(4-methoxyphenyl)methylium perchlorate ($T^+ClO_4{}^-$) were synthesized according to conventional synthetic strategies.[17] The molar enthalpy changes (ΔH_{rxn}) of the hydride transfer reactions, standard one-electron oxidation potentials, and standard one-electron reduction potentials of the corresponding species, and the reaction rate constants of the hydride transfer reactions in acetonitrile[17] were determined. The detailed results are summarized in Table 1 and Table 2.



Scheme 1.

To elucidate the most likely mechanism of hydride transfer from G-XH$^-$ to T$^+$ in acetonitrile, the thermodynamic analysis

Table 1. Molar enthalpy changes and redox potentials of the related species in acetonitrile at 298 K (Scheme 2)

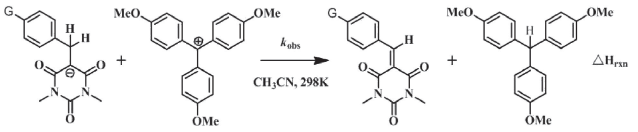
Species	$\Delta H_{rxn}{}^a$ /kcal mol^{-1}	$E_{ox}(ZH)^b$/V		$E_{red}(Z^+)^b$/V	
		CV	OSWV	CV	OSWV
G-XH$^-$					
p-CH_3O	−31.3	−0.231	−0.261	−1.510	−1.481
p-CH_3	−31.1	−0.223	−0.253	−1.471	−1.445
p-H	−30.7	−0.210	−0.240	−1.412	−1.382
p-Br	−29.9	−0.191	−0.221	−1.321	−1.296
p-NO_2	−28.9	−0.146	−0.176	−1.126	−1.097
TH		1.139	1.105	−0.627	−0.630

[a]Obtained from the reaction heats by switching the sign. [b]Reproducible to 5 mV or better.

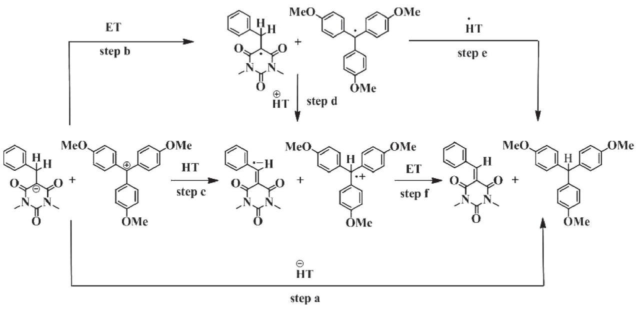
Table 2. Rate constants of the hydride transfer from G-XH$^-$ to T$^+$ in acetonitrile at 298 K together with the corresponding activation energetics and KIE (Scheme 2)

G-XH$^-$	$10^{-2} \times k_{obs}{}^a$	ΔG^b /kcal mol^{-1}	$10^{-2} \times k_{(D)}{}^c$	KIE^d
p-CH_3O	1.16	16.00	1.01	1.3
p-CH_3	0.89	16.16	0.77	1.4
p-H	0.77	16.25	0.69	1.3
p-Br	0.39	16.65	0.36	1.2
p-NO_2	0.17	17.15	0.16	1.1

[a]The unit is $M^{-1}\,s^{-1}$ and the experimental error is within 5%. [b]Obtained from Eyring equation and the uncertainty is smaller than 0.05 kcal mol^{-1}. [c]One of the two H atoms was changed by the D atoms; the unit is $M^{-1}\,s^{-1}$ and the experimental error is within 5%. [d]Obtained from KIE = $k_{obs}/(2k_{(D)} - k_{obs})$.



Scheme 2.



Scheme 3.

Table 3. Energetics of each mechanistic step of the hydride transfer reactions from G-XH$^-$ to T$^+$ shown in Scheme 3 (kcal mol^{-1})^a

Groups	ΔH (or ΔG)					
	step a	step b	step c	step d	step e	step f
p-CH$_3$O	−31.3	8.5	28.4	59.7	−39.8	−59.7
p-CH$_3$	−31.1	8.7	27.8	58.9	−39.8	−58.9
p-H	−30.7	9.0	26.7	57.4	−39.7	−57.4
p-Br	−29.9	9.5	25.5	55.4	−39.4	−55.4
p-NO$_2$	−28.9	10.5	22.0	50.9	−39.4	−50.9

^{a}The state energy changes are scaled by using enthalpy changes for steps c–e and by using free energy changes for steps b and f.

platform[12] on the possible mechanisms was first constructed (Scheme 3), and the change of the standard state energy of each reaction step (Table 3)[18] can be estimated according to eqs 4–9, of which eqs 6–9 were derived from three suitable thermodynamic cycles according to Hess' law.[17]

$$\Delta H \text{ (step a)} = \Delta H_{\text{rxn}} \tag{4}$$

$$\Delta G \text{ (step b)} = -F[E_{\text{red}}(\text{T}^+) - E_{\text{ox}}(\text{G-XH}^-)] \tag{5}$$

$$\Delta H \text{ (step c)} = \Delta H_{\text{rxn}} - F[E_{\text{red}}(\text{G-X}) - E_{\text{ox}}(\text{TH})] \tag{6}$$

$$\Delta H \text{ (step d)} = \Delta H_{\text{rxn}} - F[E_{\text{red}}(\text{G-X}) - E_{\text{ox}}(\text{TH})] + F[E_{\text{red}}(\text{T}^+) - E_{\text{ox}}(\text{G-XH})] \tag{7}$$

$$\Delta H \text{ (step e)} = \Delta H_{\text{rxn}} + F[E_{\text{red}}(\text{T}^+) - E_{\text{ox}}(\text{G-XH})] \tag{8}$$

$$\Delta G \text{ (step f)} = F[E_{\text{red}}(\text{G-X}) - E_{\text{ox}}(\text{TH})] \tag{9}$$

From Table 3, it is clear that for the five hydride transfer reactions, the state energy change of step c (28.4–22.0 kcal mol^{-1}) is a quite large positive value. Therefore, it is reasonable that the process of hydrogen atom transfer (step c) can be ruled out as the initial step.

This was also confirmed by the comparison of the state energy changes of the three possible initial steps and the activation energies (Figure 1). Because the activation energies of the reactions are much smaller than the corresponding standard state energy changes of the initial hydrogen transfer, but larger than those of the concerted hydride transfer (step a) or the electron transfer (step b), the initial hydrogen atom transfer as the isolated reaction step is impossible according to one of the most fundamental reaction laws that the activation energy is always larger than or at least equal to the corresponding standard state energy change for any elementary reaction.

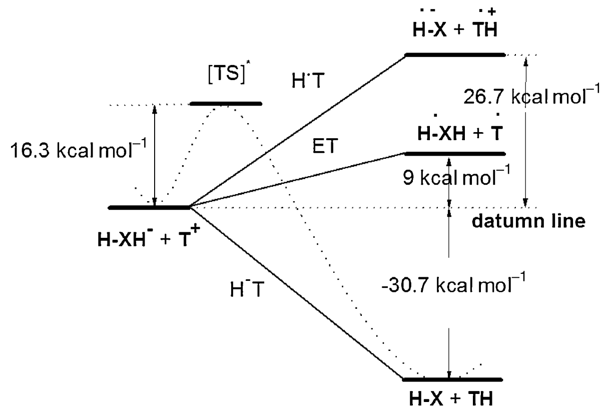


Figure 1. Comparison of state energy changes for the three possible initial steps of the hydride transfer from H-XH$^-$ to T$^+$ and the activation energy of the hydride transfer in acetonitrile.

Because the state energy change of step a is a quite large negative value and that of step b is a positive value, it seems to be that the one-step hydride transfer (step a) should be the most likely process. However, the mass of an electron is much smaller than that of the hydrogen atomic nucleus (proton), and the electron transfer should be more favorable than the proton transfer, which can receive the strong support from the Franck–Condon principle.[19] This is also to say that the mechanism is due to the energetic of the initial electron transfer rather than that of the overall hydride transfer, which was already verified and accepted by most chemists.[20] In addition, summarizing the existing experimental facts, Cheng suggested that the one-step hydride transfer mechanism is impossible when the energetic of the initial electron transfer is much smaller than 23.1 kcal mol^{-1}.[21] Therefore, on the basis of these theoretical foundations and empirical rules, the only possible initial step for the overall hydride transfer, whose initial electron transfer energetic is much smaller than 23.1 kcal mol^{-1}, is the electron transfer. Similarly, the quite large value of the state energy changes for step d (PT) as well as the comparison of the state energy changes for step d and the activation energies of the hydride transfer reactions also ruled proton transfer out as the second step of the overall hydride transfer. Therefore, the only possible second step for the overall hydride transfer from G-XH$^-$ to T$^+$ is the hydrogen atom transfer.

In fact, this multistep (e-H) mechanism could be further verified by the value of KIE (about 1, in Table 2) when H and D atoms were used as the isotopic atoms. This means that the rate-determining step does not involve the transfer of the H nucleus. Thus, it can be concluded that step a, step c, or step d is impossible as the rate-determining step.

On the basis of the above, the only possible mechanism is the electron transfer followed by the hydrogen atom transfer.

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17 The details are listed in the Supporting Information. Supporting Information is available electronically on J-STAGE.
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