*Articles*

# Theoretical Study on the Kinetics of Electron Transfer for Bond-breaking Reaction

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To test the theory of dissociative electron transfer, a simple model describing the kinetics of electron transfer bond-breaking reactions was used. The Hamiltonian of the system was given. The homogeneous and heterogeneous kinetic data fit reasonably well with an activation-driving force relationship derived from the Marcus quadratic theory. In the heterogeneous case, there is a good agreement between the theoretical calculation and the experimental result, while in the homogeneous case, a good agreement is only observed for the tertiary halides. This is due to the stability of tertiary radical resulting from the sterical effect.

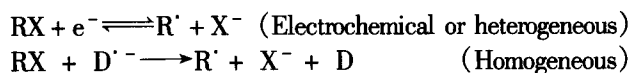**Keywords**    electron transfer, bond-breaking reaction, butyl halide

## Introduction

Free radical formation from halogenated hydrocarbons has received considerable attention because of its scientific and environmental relevance.[1-6] This reaction seems to play an important role in various processes. Bond-breaking reaction is a powerful synthetic tool to provide alkyl radicals in molecular biology processes. Electron transfer (ET) in organic molecules RX is often accompanied by bond cleavage with the formation of a radical, R·, and an anion, X⁻ (scheme 1).[7-10]

RX stands not only for alkyl halides but also for any molecule in which group X leaves after electron transfer, thus, this process involves bond breaking. R is the "remaining group", *i.e.*, the group remaining with an unpaired electron. $D/D^{·-}$ is a chemically stable redox couple and with the reaction take place in an outer-sphere manner, it does not involve any bond breaking process.

**Scheme 1**

$$RX + e^- \rightleftharpoons R^· + X^- \quad \text{(Electrochemical or heterogeneous)}$$
$$RX + D^{·-} \longrightarrow R^· + X^- + D \quad \text{(Homogeneous)}$$

Marcus theory of outer-sphere ET[11] gave a description of the activation process in terms of two main factors: the reorganization of the solvent and the internal reorganization of the molecule (changes in bond angles and lengths). The treatment of solvent reorganization like the Marcus-Hush fashion leads to a quadratic activation force relationship[11-14] for both homogeneous and heterogeneous electron transfers.

$$\Delta G^{\#} = \Delta G_0^{\#} \left[ 1 + \Delta G^0/(4\Delta G_0^{\#}) \right]^2 \qquad (1)$$

$\Delta G^{\#}$, free energy of activation for the forward reaction; $\Delta G^0$, free energy of the reaction. The intrinsic barrier free energy, $\Delta G_0^{\#}$, *i.e.*, the free energy of activation at zero driving force ($-\Delta G^0$) includes two terms.

$$\Delta G_0^{\#} = (D_{RX} + \lambda_o)/4 \tag{2}$$

where $D_{RX}$ is the dissociation energy and $\lambda_o$ is the solvent reorganization energy. The activation free energies are obtained in terms of the Morse potential function and shown in the following. Butyl halides are investigated as typical model compounds to test the theoretical model.

## Hamiltonian of the system

Let $\varepsilon_a$ be the vacuum energy level of an antibonding orbital of the RX molecule and $\varepsilon_k$ be the energy level of an occupied orbital. When the antibonding orbital is occupied by an electron, the RX molecule will break up into its respective fragments R· and X⁻. The Hamiltonian describing the system consists of three parts:

$$H = H_{elec} + H_{solv} + H_{bb} \tag{3}$$

$$H_{elec} = \varepsilon_a n_a + \sum_k \varepsilon_k n_k + \sum_k [V_k c_k^+ c_a + V_k^+ c_a^+ c_k] \tag{4}$$

where $n_a$ is the occupating number operator of the antibonding orbital, and $c_a^+$ and $c_a$ are creation and annihilation operators, respectively. $H$ denotes the Hamiltonian energy. The electronic states on the metal are labeled by the quantum number $k$, and $n_k$, $c_k^+$ and $c_k$ denote the corresponding occupied number, creation and annihilation operators. The $V_k$ and $V_k^+$ are the corresponding matrix elements.

The solvent part is:

$$H_{solv} = \frac{1}{2}\sum_v \hbar\omega_v(P_v^2 + q_v^2) - n_a\sum_v \hbar\omega_v g_v q_v \tag{5}$$

where the first term denotes the unperturbed solvent, $p_v$ and $q_v$ are the momenta and the dimensionless coordinates respectively, $\omega_v$ is the frequencies and labels the solvent modes, and $\hbar = h/2\pi$. The second term accounts for the interaction, assumed linear in the change $n_a$ with $g_v$ as the interaction constant.

The term $H_{bb}$ describes that the broken of the bond is due to the antibonding orbital occupied by a metal electron. As in Saveant's model, they describe the R—X bond by a Morse potential and the interaction between the fragments R· and X⁻ by the repulsive part of the same Morse potential. By multiplying these potentials by the

operators $[1 - n_a]$ and $n_a$, respectively, they construct an effective switching function describing the bond breaking process:

$$H_{bb} = D[1 - n_a]\{1 - \exp[-\beta(r - r_0)]\}^2 + Dn_a \\ \exp[-2\beta(r - r_0)] \tag{6}$$

where $r$ is the bond distance, $r_0$ the equilibrium bond distance and $D$ the dissociation energy. The parameter $\beta$ relates to the bond vibration frequency $\omega_b$ (in s⁻¹), i.e., $\beta = \omega_b(\mu/2D)^{1/2}$, in which $\mu$ is the reduced mass of the atoms participating in the bond broken process.

## Results and discussion

### *Electrochemical reduction of butyl halides*

The main factor governing the thermodynamics and kinetics of the reductive cleavage is the dissociation energy of the breaking bond. The bond length is only determined by the geometry of the equilibrium state, but the bond dissociation energy is related with the equilibrium state and the infinite dissociation state. It is assumed that there is a transition state between the equilibrium state and the bond broken state. But the determination of the transition state is a more difficult task. There is a crossing point of the non-adiabatic energy curves between the neutral molecule and its corresponding anion radical. The energy difference between the nonadiabatic activation state (at the crossing point) and the adiabatic activation state (at the actual transition state) denotes the coupling of the two energy potential curves, i.e., the coupling matrix element [$V_k$, in Eq. (4)]. This idea is proved to be accurate in previous literature.[15-17]

In the electrochemical case, the relation between the reorganization energy ($\lambda_o^{het}$) and $1/a$ is approximated by

$$\lambda_o^{het} = 3.15/a \tag{7}$$

and where $a$ is estimated by

$$a = a_X(2a_{RX} - a_X)/a_{RX} \tag{8}$$

Here, $a_X$ is the radius of the halogen (X), and its estimated value has been obtained by using arithmetic mean method.[14] The $a_{RX}$ is the radius of the whole molecular sphere, which is derived from the molar mass (M) and

the density $(\rho)$, that is, $a_{RX} = (3M/4N_A\rho)^{1/3}$, in which $N_A$ is the Avogadro's constant. From the obtained values of $\lambda_0^{het}$ and the values of the bond dissociation energy from the literature,[18] the theoretical values of the intrinsic barrier, $i.e.$, $\Delta G_0^{\#}$ (theor), is obtained in terms of Eq. (2), listed in Table 1.

$\Delta G_{het}^{\#}$(exp), the free energy of activation of the forward electron transfer at the peak potential $(E_p)$ is

$$\Delta G_{el}^{\#} = \frac{RT}{F} \ln Z^{het} \left(\frac{RT}{\alpha_p F v_s D}\right)^{1/2} ] - 0.78 \frac{RT}{F} \qquad (9)$$

where $D$ is the diffusion coefficient of RX, $v_s$ is the scan rate, $Z^{het}$ is the collisional frequency, $\alpha_p$ is the transfer coefficient at the peak potential and F is the Faraday's constant. Thus, the free energy of the activation will be decreased as the scan rate is increased at a fixed temperature or as the temperature is decreased at a fixed scan rate.

The transfer coefficient can be considered as an approximate constant, $\alpha$(exp) is obtained from

$$\alpha = \frac{1.85}{E_{p/2} - E_p} \times \frac{RT}{F} \qquad (10)$$

where $E$ is the potential at specified potential. The theoretical value of the free energy of activation, $\Delta G_{het}^{\#}$(theor), can be obtained from Eq. (11)

$$\Delta G_{\pm 1}^{\#} = \Delta G_{0,het}^{\#} \left[ 1 \pm F \frac{E_p - E_{(RX/R^{\cdot} + X^-)}^0 - \phi_r}{4\Delta G_{0,het}^{\#}} \right]^2 \qquad (11)$$

where $\phi_r$ is the potential difference between the reaction site and the solution, which is obtained from previous measurements carried out in the same solvent (DMF).[19] The symbol $\pm 1$ represents the forward and the backward reaction, respectively. Once $\Delta G_{het}^{\#}$ (exp) is known, $\Delta G_0^{\#}$(exp) is obtained from Eq. (1) as

$$\Delta G_0^{\#}(\exp) = \{ [ (E_p - E^0 - \phi_r - 2\Delta G_{het}^{\#})^2 - (E_p - E^0 - \phi_r)^2 ]^{1/2} - (E_p - E^0 - \phi_r - 2\Delta G_{het}^{\#}) \}/4 \qquad (12)$$

The results are displayed in Table 1. It can be seen that

there is a quite satisfactory agreement between the theoretical and the experimental values when $\Delta G_4^0 = 0$, but the agreement from the second estimation $(\Delta G_4^0 \neq 0)$ is not as good as that from the case of $\Delta G_4^0 = 0$, where $\Delta G_4^0$ is the standard Gibbs free energy of the reaction:

$$RX + R^{\cdot DMF} \longrightarrow RX^{DMF} + R^{\cdot g}$$
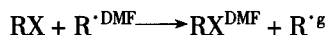
The comparison among $\alpha$(exp), $\alpha$(pred) and $\alpha$(theor) values also testifies the dissociative electron transfer theory. The transfer coefficient $\alpha$ is expected to decrease upon raising the driving force in a linear way:

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\#}}\right) = \frac{1}{2}\left(1 + F\frac{E_p - E^0 - \phi_r}{4\Delta G_0^{\#}}\right) \qquad (13)$$

$\alpha$(pred) is the value obtained from Eq. (13) using $\Delta G_0^{\#}$ (exp), whereas $\alpha$ (theor) is obtained from Eq. (13) using $\Delta G_0^{\#}$ (theor). It can be seen from Table 1 that, although $\alpha$(pred) is somewhat larger than the experimental values, the reason that the transfer coefficient is distinctly below 0.5 thus appears to be the fact that the reduction potential is much negative relative to the standard potential. The potential dependent heterogeneous rate constant $k$, according to Marcus theory of outer-sphere electron transfer, is related to the activation free energy, $\Delta G^{\#}$, by the following

$$k = Z^{het} \exp(-\Delta G_{het}^{\#}/RT)$$

In fact, the identification of the pre-exponential factor with the collision frequency is certainly a crude approximation, but to some extent, it is valuable to show the variable trend of the rate constant. $\Delta G_{het}^{\#}$(theor) is in better agreement with the first case than with the second case. The free energy of activation of the reverse reaction, $\Delta G_{-1}^{\#}$, is much larger than that of the forward reaction, $\Delta G_{+1}^{\#}(\Delta G_{het}^{\#})$, showing that it is impossible to take place for the backward reaction.

### Homogeneous reduction of butyl halides

These reactions can be thought of as a sequence of elementary steps: the diffusion of the two reagents to form the precursor complex, then the activation of the precur-

**Table 1**   Kinetics of the heterogeneous reduction cleavage of butyl bromides and iodides[a, b]

| Compd. | BuI | | | BuBr | | |
|---|---|---|---|---|---|---|
| | $n$-BuI | $sec$-BuI | $t$-BuI | $n$-BuBr | $sec$-BuBr | $t$-BuBr |
| $-E^0(V)^c$ | 1.075(1.209) | 0.946(1.080) | 0.826(0.960) | 1.109(1.230) | 1.049(1.190) | 0.929(1.050) |
| $Z^{het}(cm/s)$ | $4.5 \times 10^4$ | $4.5 \times 10^4$ | $4.5 \times 10^4$ | $4.5 \times 10^4$ | $5.1 \times 10^4$ | $4.5 \times 10^4$ |
| $a_{RX}$ | 0.356 | 0.358 | 0.362 | 0.350 | 0.350 | 0.354 |
| $a_X$ | 0.304 | 0.305 | 0.306 | 0.282 | 0.282 | 0.283 |
| $a$ (nm) | 0.348 | 0.350 | 0.353 | 0.337 | 0.337 | 0.340 |
| $\lambda_0^{het}$ (eV) | 0.905 | 0.902 | 0.892 | 0.935 | 0.935 | 0.927 |
| $D_{RX}(eV)^d$ | 2.56 (2.67) | 2.38 (2.49) | 2.20 (2.31) | 3.00 (3.12) | 2.99 (3.07) | 2.87 (2.99) |
| $-E_p(V)$ | 2.33 | 2.05 | 1.91 | 2.85 | 2.63 | 2.51 |
| $-\phi_r$ (V) | 0.09 | 0.084 | 0.081 | 0.102 | 0.097 | 0.090 |
| $\Delta G_0^{\#}$ (theor)$^e$ | 0.866(0.894) | 0.796(0.848) | 0.773(0.801) | 0.984(1.014) | 0.982(1.001) | 0.949(0.979) |
| $\Delta G_0^{\#}$ (exp)$^e$ | 0.864(0.817) | 0.808(0.760) | 0.802(0.751) | 1.043(1.000) | 0.987(0.936) | 0.993(0.949) |
| $\Delta G_{het}^{\#}$(theor)$^e$ | 0.381(0.453) | 0.368(0.463) | 0.353(0.425) | 0.335(0.397) | 0.380(0.442) | 0.350(0.414) |
| $\Delta G_{het}^{\#}$(exp)$^e$ | 0.380 | 0.379 | 0.379 | 0.385 | 0.385 | 0.388 |
| $\Delta G_{-1}^{\#}$(exp)$^e$ | 1.546(1.484) | 1.388(1.349) | 1.356(1.294) | 1.974(1.915) | 1.864(1.785) | 1.841(1.784) |
| $\alpha$ (theor) | 0.332(0.354) | 0.340(0.369) | 0.337(0.364) | 0.292(0.313) | 0.311(0.332) | 0.303(0.325) |
| $\alpha$ (pred) | 0.331(0.341) | 0.342(0.357) | 0.343(0.355) | 0.303(0.310) | 0.312(0.321) | 0.312(0.319) |
| $\alpha$ (exp) | 0.30 | 0.33 | 0.32 | 0.25 | 0.25 | 0.20 |

[a] In DMF, at a glassy carbon electrode at 10 ℃. The scan rate $v = 0.1$ V/s. The values are in the parentheses when $\Delta G_4^0 \neq 0$. [b] $D = 10^{-5}$ cm$^2$/s; [c] $\Delta G_4^0$: standard Gibbs free energy of the reaction RX + R$^{\cdot DMF}$→ RX$^{DMF}$ + R$^{\cdot g}$; $\Delta G^0$, $E^0$: standard free energy, standard potential of the reaction RX + e$^-$→ R$^{\cdot}$ + X$^-$. [d] From literature thermochemical data in Ref. 16. [e] In eV.

sor complex to yield the successor complex, at last the separation of this latter complex into the products [Eq. (14)].

$$RX + D^{\cdot -} \rightleftharpoons (RX \mid D^{\cdot -}) \rightleftharpoons (RX^{\cdot -} \mid D)$$
$$\rightleftharpoons R^{\cdot} + X^- + D \qquad (14)$$
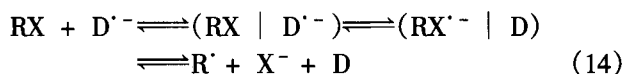
The same strategy as in the electrochemical case was followed here. For the cross-exchange reaction between RX and D$^{\cdot -}$[11a]

$$\lambda_0^{hom} = e^2 \left( \frac{1}{\varepsilon_{OP}} - \frac{1}{\varepsilon_S} \right) \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \qquad (15)$$

where $a_1$ and $a_2$ are the radii of the spheres equivalent to the RX and D molecules, and $d$ is the distance of their centers in the precursor complex, whereas the experimental value of $\Delta G_0^{\#}$ is then derived from Eq. (1) by means of

$$\Delta G_0^{\#} = \{ [(\Delta G^0 - 2\Delta G^{\#})^2 - (\Delta G^0)^2]^{1/2} - (\Delta G^0 - 2\Delta G^{\#}) \} / 4 \qquad (16)$$

where $\Delta G^0 = -nF[E_{RX/(R^{\cdot}+X^-)}^0 - E_{D/D}^{0\cdot -}]$   (17)

($E_{D/D}^{0\cdot -}$ is the standard potential of the mediator couple, $n = 1$). The experimental free energy of activation is obtained from the rate constant. The theoretical prediction of the free energy of activation is thus obtained from Eq. (18).

$$\Delta G_{hom}^{\#} = \Delta G_{0,hom}^{\#} \left( 1 + \frac{\Delta G^0}{\Delta G_{0,hom}^{\#}} \right)^2 \qquad (18)$$

All the results are shown in Table 2. However it distinctly appears that, given the halogen and the nature of the reacting carbon, the agreement is better for the tertiary halides than that for the secondary or the primary halides. $\Delta G_0^{\#}$ (theor) became larger and larger from the tertiary to the secondary or the primary, but the trend is opposite to $\Delta G_0^{\#}$ (exp). Thus, taking the theory-experiment agreement of the tertiary halides as reference, it can be seen that the theory overestimates $\Delta G_0^{\#}$ and $\Delta G^{\#}$ in the case of secondary and primary halides, even though the difference remains small (about 50 mev at maximum except $n$-BuI and $sec$-BuI).

The homogenous rate constant thus can be derived from Eq. (19).

**Table 2** Kinetics of the homogeneous reduction of butyl halides by aromatic anion radicals[a, b]

| Compd. | $n$-BuI[c] | $sec$-BuI | $t$-BuI | $n$-BuBr[c] | $sec$-BuBr | $t$-BuBr | $n$-BuCl[c] | $sec$-BuCl | $t$-BuCl |
|---|---|---|---|---|---|---|---|---|---|
| $-E_{RX/(R^{\cdot}+X^-)}$ (V) | 1.075 | 0.946 | 0.826 | 1.109 | 1.049 | 0.929 | 1.267 | 1.258 | 1.138 |
| $-E_D$ (V) | 1.900[d] | 1.730[e] | 1.730[e] | 1.900[d] | 1.900[d] | 1.900[d] | 2.540[f] | 2.540[f] | 2.540[c] |
| $\lambda_0^{hom}$ (eV) | 0.633 | 0.631 | 0.628 | 0.656 | 0.656 | 0.653 | 0.674 | 0.672 | 0.668 |
| $D_{RX}$ (eV) | 2.56 | 2.38 | 2.20 | 3.00 | 2.99 | 2.87 | 3.50 | 3.45 | 3.42 |
| $-\Delta G^0$ (eV) | 0.825 | 0.784 | 0.904 | 0.766 | 0.851 | 0.971 | 1.273 | 1.282 | 1.402 |
| $\Delta G^{\#}$ (theor)[g] | 0.439 | 0.412 | 0.327 | 0.561 | 0.536 | 0.462 | 0.505 | 0.490 | 0.441 |
| $\Delta G^{\#}$ (exp)[g] | 0.322 | 0.395 | 0.345 | 0.523 | 0.490 | 0.466 | 0.477 | 0.460 | 0.432 |
| $\Delta G_0^{\#}$ (theor)[g] | 0.798 | 0.753 | 0.707 | 0.914 | 0.912 | 0.885 | 1.044 | 1.031 | 1.022 |
| $\Delta G_0^{\#}$ (exp)[g] | 0.671 | 0.735 | 0.726 | 0.874 | 0.863 | 0.885 | 1.014 | 0.998 | 1.012 |
| $k_{hom}$ (theor)[g] | $8.50 \times 10^3$ | $1.39 \times 10^4$ | $4.54 \times 10^5$ | 67.95 | 86.41 | $1.79 \times 10^3$ | $6.24 \times 10^2$ | $5.69 \times 10^2$ | $4.24 \times 10^3$ |
| $k_{hom}$ (exp)[g] | $8.73 \times 10^5$ | $2.79 \times 10^4$ | $2.17 \times 10^5$ | $3.06 \times 10^2$ | $5.69 \times 10^2$ | $1.52 \times 10^3$ | $1.89 \times 10^3$ | $1.95 \times 10^3$ | $6.13 \times 10^3$ |

[a] In DMF; temperature, 10 ℃. [b] All standard potentials in V vs. SCE (Ag/AgCl). [c] Temperature, 20 ℃. [d] The mediator is anthracene. [e] The mediator is 4-cyanopyridine. [f] The mediator is biphenyl. [g] In eV.

$$k = Z^{hom} \exp\left(-\Delta G_{hom}^{\#}/RT\right) \qquad (19)$$

For the whole series of homogeneous mediators, $Z^{hom}$ value was found to equal to $3 \times 10^{11}$ $(M \cdot s)^{-1}$. From the data of homogeneous rate constant, it is obvious that the agreement between the theoretical and experimental values is much better for the tertiary halides than for the secondary or the primary halides and the rate constant of the tertiary halide is much larger than that of the secondary or of the primary. These observations suggest that in the absence of strong steric hindrance, the tertiary halides are easy to break the C—X bond and to form the tertiary radicals, which also prove the fact that the tertiary radical is more stable than the secondary or the primary radical.

## Conclusions

The homogeneous and heterogeneous processes accord with a quadratic activation-driving force free energy relationship, with the intrinsic barrier being the sum of two contributions. In the electrochemical case, there is a good agreement between the theoretical and experimental values of the intrinsic barrier for all the butyl iodides and bromides. In the homogeneous case, there is also a good agreement between theoretical predictions and experiment in the case of tertiary butyl. The homogeneous reduction of tertiary butyl halide is faster than that of secondary or primary butyl halide, which shows that the tertiary butyl radical is more stable than the secondary or primary radical.

## Acknowledgement

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