The Nature of the Intrinsic Barrier in Methyl Transfer Reactions

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The intrinsic barrier in the methyl transfer reaction $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$ has been shown to vary quadratically with the C-X distance $d$; linear dependence of the intrinsic barrier on the deformation energies or methyl cation affinities of the substrate, CH$_3$X, should therefore hold only approximately in a narrow range of structural variations in X.

**Introduction**

The intrinsic barrier, $\Delta E'_*$ (or $\Delta G'_*$), has played an essential role in the interpretation of experimental reactivity data$^1$ for gas phase methyl transfer reaction, (1).

$$ \text{X}^- + \text{CH}_3\text{Y} \rightleftharpoons \text{XCH}_3 + \text{Y}^- \quad (1) $$

According to the Marcus equation$^2$, (2)

$$ \Delta E'_{\text{TS}} = \Delta E'_* + \frac{1}{2} \Delta E'' + \frac{(\Delta E'')^2}{16 \Delta E'_*} \quad (2) $$

where $\Delta E'_{\text{TS}} = \frac{1}{2} (\Delta E'_{XX} + \Delta E'_{YY})$, the intrinsic barrier is the activation barrier, $\Delta E'_{\text{TS}}$ (or $\Delta G'_{\text{TS}}$), that would exist in the absence of any thermodynamic driving force, i.e., when $\Delta E'_{\text{TS}}$ (or $\Delta G'_{\text{TS}}$) = 0. Wolfe et al.$^{3}$ correlated the intrinsic barrier with the deformation energy, $\Delta E_{\text{depl}}$, required to distort the substrate CH$_3$Y from its ground state to its transition state(TS) geometry.

On the other hand, a satisfactory linear correlation was obtained between the intrinsic barrier and the gas phase methyl cation affinity (MCA) of the nucleophile$^{15}$, (3).

$$ \text{CH}_3\text{Y} \rightleftharpoons \text{CH}_3^+ + \text{Y}^- \quad (3a) $$

$$ \text{MCA(Y^-)} = \Delta H_{\text{int}} + D^* (\text{CH}_3 - \text{Y}) - \text{EA(Y)} \quad (3b) $$

$$ + \text{IP} (\text{CH}_3) $$

where $D^*$, EA and IP are the homolytic bond dissociation energy, electron affinity and ionization potential of the respective species shown in the parentheses. Despite of these illuminating works on the intrinsic barrier of methyl transfer reactions, its true nature is still elusive.

The principle of microscopic reversibility in reaction kinetics requires an identity methyl transfer reaction i.e., $X = Y$ in eq (1), to have a symmetrical transition state of a trigonal bipyramidal five-coordinate (TBP-5C) structure.

In this work, we will show that the intrinsic barrier is simply a quadratic function of the C-X distance in the TBP-5C structure as defined in Figure 1.

We have carried out ab initio MO calculations at the 4-31G level$^4$ to determine energies of the TBP-5C structure formation, $\Delta E'_*(\text{TBP-5C})$ in eq(4), at various C-X distances $d$, (1), for $X = H$ and F.

$$ \Delta E'_{\text{TBP-5C}} = E(\text{TBP-5C}) - E(R) \quad (4) $$

where $E(R)$ is the energy of reactants in solution phase or of reactant cluster in gas phase, (Figure 1).

$$ \begin{array}{c}
\text{H} \\
\text{X} \\
\text{H}
\end{array}
\begin{array}{c}
\text{C} \\
\text{H}
\end{array}
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{d}
\end{array}
 \begin{array}{c}
\text{d}
\end{array}
$$

The energies were minimized at fixed $C_3v$ symmetry and $d$. The choice of $X = H$ and F has been dictated by their distinct soft (H) and hard(F) behaviors as nucleophiles$^6$. Variations of $\Delta E'_*$ i.e., $\delta \Delta E'_*$ (which is in this case equal to $\delta E(\text{TBP-5C})$), with $d$ gave parabolic potential energy curves, Figure 2, as one might have expected. These curves show that $\delta \Delta E'_*$ can be represented by a simple harmonic oscillator model, (5).

$$ \delta \Delta E'_* = \frac{1}{2} k (d - d_0)^2 $$

**Figure 1.** Definition of $\Delta E'_*(\text{TBP-5C})$-E(R) where TBP-5C and R are trigonal bipyramidal five-coordinate and reactants (in solution phase) or reactant cluster (in gas phase), respectively.

**Figure 2.** Variation of $\Delta E'_*(\text{TBP-5C})$ vs the relative C-X distance $\Delta d(d-o)$ for $X = H$ (o) and F(x).
where $k$ and $d$ are the force constant and the distance of the minimum energy, respectively. The portion of the curve (Figure 2) in the region $d \neq d_c$, should represent energy required to stretch or expand the C-X further from $d_c$, until the system, (I), dissociates into $\text{CH}_4^+ + 2\text{X}^-$ eventually; thus this part constitutes an expansion region. In contrast the curve in the region $d < d_c$ represents energy required to compress the C-X, and hence constitutes a compression region.

In the expansion (E) region, bond breaking has progressively less bond formation and the loose TBP-5C structure will have positive charge on the methyl carbon, whereas in the compression (C) region bond formation increases progressively as $d$ decreases (in (I) $d$ is much greater than the normal C-X bond length since (I) represents the TS structure, so that compression does not lead to the $d$ less than the normal bond length) and bond formation becomes greater than bond breaking in a tight TBP-5C structure with negative charge on the methyl carbon. On the whole, the potential energy curve is parabolic, but within a sufficiently narrow range of $d$ variation in either E or C region the $\delta A^*_{E}$ can be taken as linear with $d$. Thus reactivity trends within the E region will respond to the leaving group ability, respectively whereas those within the C region will respond to the nucleophilicity of $X^-$.  

Now let us suppose we have a series of $X$ (e.g. $X_0$, $X_1$, $X_2$, ...), etc) with relatively minor structural variations, so that we may approximate the force constant for the C-X stretching as practically constant within the series, i.e., $k_0 = k_1 = k_2 = ...$. The structural variation of $X$ will now influence only on $d$ (i.e., $d_0$, $d_1$, $d_2$, ...etc) in the formation of TBP-5C structure and the variation of the intrinsic barrier, $\delta A^*_{E}$ with the structural variation will then depend only on $d$ and will have a quadratic form similar to the curves shown in Figure 2 for anionic nucleophiles $X$ of 2nd row elements, $\text{OH}^-$, $\text{F}^-$, $\text{CN}^-$, $\text{NC}^-$, variations in $d$, $\Delta d$, were much greater than those in $k$, $\Delta k$.

$\Delta d^2 \geq (4 \sim 10) \Delta k$.

Theoretically $k$, is defined as $k = (\frac{\partial^2 A^*_{E}}{\partial d^2})_0 d$ where $R_i = d_i$. $d_0$ and $k_0$ is evaluated at an extremum point, i.e., at $d_i = d_0$. Application of Badger's rule, $d_i = a \log k_i$, indicates $k_i$ is approximately constant within the series, since $a$ and $b$ are the universal constants. Thus variations in deformation energy can be attributed mainly to $\Delta d$; for the series of $X$ the relative formation energy of the TBP-5C(TS) structure and hence $\delta A^*_{E}$ can therefore be expressed as $\delta A^*_{E} = \text{const} \cdot (d - d_0)^2$. There will be a member in the series which has the minimum energy of $A^*$ or $\delta A^*$ corresponding to the C-X distance of $d_0$, i.e., $d = d_0$. However, for a wide spectrum of structural variation in $X$, and hence in $d$, we can not expect the force constant $k$ to be constant over the whole range; the approximation of $k = \text{constant}$ will hold over a relatively narrow range and hence we will be normally concerned with a small portion of the curves in Figure 2. Thus in practice we may encounter three types of $\delta A^*$ dependence on structural parameters: (i) A series within $E$ region in which case an approximate linear correlation between $\delta A^*_{E}$ and a structural parameter of $X$, e.g. the Hammett substituent constant $\sigma$, may result. (ii) As an intermediate case, we may have a series in which the variation of $\delta A^*_{E}$ covers both $E$ and $C$ regions in the close proximity of the energy minimum, i.e., around $d_c$. In this case we would expect no linear correlation between $\delta A^*_{E}$ and $\sigma$, since a parabolic nature of the curve will prevail (Figure 2). (iii) Lastly we can think of a series within $C$ region. However it is highly improbable that we find any examples belonging to this category, since the $d$ is so short that no such highly associated form is possible due to strong exchange repulsions.

We will present examples belonging to the first two categories of $\delta A^*$ dependence on $\sigma$.

(i) $\text{XCH}_4 + \text{OH}^- \rightarrow \text{OH}^- \text{CH}_3 \text{OSO}_4 \text{CH}_4 \text{X}$

(ii) $\text{XCH}_4 \text{OSO}_4 \text{CH}_4 + \text{OSO}_4 \text{CH}_4 \text{X}$

$\delta \Delta G^* = -1.02 \sigma$  

Thus we can see that this series covers a small portion of the $E$ region ($\delta \Delta G^* \approx 1.0 \text{ kcal/mol}$); the intrinsic barrier decreases as $\sigma$ increases and hence $\text{OSO}_4 \text{CH}_4 \text{X}$ with $X = \text{MeO}$ has the highest barrier with a loose TBP-5C TS (longest $d$), (II), while that with $X = 3, 4$-Cl$_2$ has the lowest barrier with a relatively tight TBP-5C (shortest $d$), (III), compared with other arenensulfonates studied.

(ii) Two interesting examples belonging to this category are:

(a) $\text{XCH}_4 \text{H}_S^- \rightarrow \text{CH}_3 \text{SCCH}_4 \text{X}$

(b) $\text{XCH}_4 \text{H}_S \text{CH}_4^- \rightarrow \text{SCCH}_4 \text{H}^+$

$\delta \Delta G^* = 0.7 \text{ kcal/mol}$ with a relatively tight TS and negative charge on the methyl carbon. The distance $d$ decreases, however, progressively from $X = 3, 4$-Cl$_2$ (electron-withdrawing group) down to $X = \text{p-t-Bu}$ (electron donating group) in $\text{XCH}_4 \text{H}_S$ with an approximately medium value of $d$, i.e., $d = d_c$ for the unsubstituted thiophene.

Figure 3. Plot of $\delta \Delta G^*$ vs $\sigma$ for Methyl transfers between substituted thiophenoxides.
Figure 4. Plot of $\Delta E_f$ vs $\sigma^0$ for Cl$^-$ exchanges in substituted benzyl chlorides.

Note that in loose type of TS's within E region (example i) a better leaving group has a relatively tight TBP-5C structure, whereas in tight TS's covering both C and E regions (example ii) a better leaving group has relatively loose TBP-5C structure. These types of behaviors are also found in other reactions and indeed seem to occur in general.

$^{11}$Cl$^- + YC_6H_5CH_2Cl \rightleftharpoons$ CI$^-C_6H_5CH_2Y + Cl^-$  \hspace{1cm} (9)

where $Y = p$-Me, m- Me, H, m-Cl and m-NO$_2$.

In this series, structural variations are not in X, (i), but are in the substrate. The plot of the gas phase data of $\Delta E_f$ vs $\sigma^0$ gave a distinct V shaped curve covering small portions ($\Delta E_f = 3.0$ kcal/mol) of both E and C regions, Figure 4. Here again the benzylic carbon has been shown to be negatively charged with a tight TS$^{11}$. Electron withdrawing (donating) substituents in the substrate seem to favor a relatively loose (tight) TS with the negative charge on the benzylic carbon.

Another important difference between reactions belonging to category (i) (within E region) and (ii) (covering both E and C regions) is that activation barriers (or TS structure) for cross reactions, $\Delta G_1^Y$ (eq. 2), may be linearly correlated with the intrinsic factor, $\Delta G^0_2$ ($\Delta G^0_{1X}$ or $\Delta G^0_{1Y}$ in eq. 2) in the former, whereas in the latter $\Delta G_1^Y$ cannot be correlated linearly with $\Delta G^0_2$ but may be correlated with the thermodynamic factor, $\Delta G^0$. This is because in the former both $\Delta G^0_{1X}$ and $\Delta G^0_{1Y}$ may be linear with $\sigma$, but in the latter $\Delta G^0_2$ cannot be linear with $\sigma$ as shown above. Thus reactions in the category (i) may be "intrinsic controlled", whereas those in (ii) may be "thermodynamic controlled".

Approximate linearity found between the intrinsic barrier, $\Delta E^*_{in}$ and deformation energies, $\Delta E_{def}$ for MCA$^{10}$ can easily be accounted for in the light of the results of the present studies; both $\Delta E_{def}$ and MCA are the approximations to the formation energies of the TBP-5C structure $\Delta E^*_f$ since both quantities represent only substrate part of the TBP-5C formation energies within E region. Scatters of points from the linear plots of $\Delta E^*_f$ against these quantities probably result from the relatively large variations in $k$ (for example, see Figure 2 for $k$ values in the case of $X = H$ and $F$) and also from the quadratic dependence of $\Delta E^*_f$ (TBP-5C) on the C-X distance $d$ (close examination of Fig 6 in ref 3 and Fig 2 in ref 1c reveals clear trends towards parabolic dependence of $\Delta E^*_f$ on $\Delta E_{def}$ as well as on MCA) due to wide ranges covered ($\Delta E_{def} = 45-55$ kcal/mol).

We therefore conclude that the intrinsic barrier in the methyl transfer reaction represents the formation energy of the trigonal bipyramidal five-coordinate structure, which in turn is quadratically dependent on the C-X distance within a series of $X$.

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References


9. I. Lee, Submitted for publication.
