the previous step, a ($2\pi/5$- or ($2\pi/6$-) cyclically related path is (uniquely) generated, and the pair of paths are taken as the boundaries of the canonical cell. The only ambiguity arising in this whole process involves a twofold choice for the chirality of the polyhedron and a twofold (orientational) choice for the "top" end of the cell. Thence there may be no more than $2 \times 2 = 4$ canonical unit cells for any polyhedron. This maximum number is divided by 2 if the polyhedron is achiral, and it is (further) divided by two if the polyhedron has a symmetry element interchanging "top" and "bottom" ends. Since the (frequent) presence of C_2 axes and/or reflection planes may ordinarily be readily ascertained from a cell, uniqueness is often readily determined. In the (apparently rather few) remaining cases the other cells associated to a given cell need be generated and checked against the (already complete) list of cells to identify the possibility of duplication. These equivalent canonical cells are conveniently generated by rotating the cell around so that ends and/or sides trade places, then "transforming" (as via processes in Figure 21) to obtain a canonical cell.

This overall scheme was applied to yield cells for distinct preferred-class polyhedra with $v \leq 88$. The results are as in Figures 6 and 7 and Table I. Finally, it is of some interest to note that the polyhedra of fivefold symmetry have v a multiple of 10, and those of sixfold symmetry have $v - 24$ a multiple of 12. This is seen from eq 3.6 if we note that the number of six-rings is a multiple of 5 for the case of a fivefold symmetry axis and, for the case of a sixfold symmetry axis, the excess of six-rings over the two containing the sixfold axis is a multiple of 6. These multiples of course are just the number of six-rings in a unit cell.

Registry No. Carbon, 7440-44-0; buckminsterfullerene, 99685-96-8; graphite, 7782-42-5; diamond, 7782-40-3.

How Is Transition State Looseness Related to the Reaction Barrier?

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Abstract: Using a thermodynamic approach for the reaction class $\mathrm{Y + AX \rightarrow YA + X}$, a link is drawn between barriers and transition state (TS) looseness. Thermochemical indexes are derived which allow the calculation of the thermochemical looseness of the TS from knowledge of the barriers for the forward and reverse directions ($\Delta E^{\ddagger}_{f}$, $\Delta E^{\ddagger}_{r}$). It is shown that high reaction barriers ($\Delta E^{\ddagger}_{f} + \Delta E^{\ddagger}_{r}$) are associated with thermochemically loose TSs. This correlation derives from two fundamental features of reactivity: (a) that high barriers are associated with TSs which are close to their dissociation limits, and (b) that reaction barriers derive from the deformations that are required to carry the ground-state molecules to the TS. The application is extended to solution-phase reactions, and an additional loosening effect emerges which accounts for the stability of the ions, $A^+ + X^-$. It is concluded that the thermochemical looseness involves bond distortion effects, which are dominated by the height of the barriers, and electron-density-depletion effects which are dominated by the stability of the ions. Computational and experimental data are discussed. Thermochemical looseness and geometric looseness correlate whenever bond stretchings are the main distortions which establish the TS. Thermochemical and geometric looseness will not correlate when bond stretchings are not the principal distortions which establish the TS. The lack of correlation between the two types of looseness may provide therefore, some information about the activation process. Potential application to other reactions is discussed.

The reaction rate is the direct and most rigorously defined reactivity observable. Associated with the rate is another experimental observable, the so-called reaction barrier. An elusive reactivity "observable" is the structure of the TS (transition state) which is a quest of physical organic chemistry. A fundamental question may then be posed, whether there exists any correlation between the measurable and the elusive reactivity "observables". For if such a relationship can indeed be established, it would then be possible to derive structural features of the TS directly from a measurement of reaction kinetics.

Such relationships have been previously deduced based on curve crossing principles in the context of the SCD model.[1-4] It has thus been shown that the TS of the identity $\mathrm{S_N2}$ reaction (eq 1a)

$$\mathrm{X^- + CH_3X \rightarrow XCH_3 + X^-} \tag{1a}$$

becomes looser as the barrier increases.[1-4] A similar relationship was shown to carry over to nonidentity $\mathrm{S_N2}$ reactions (eq 1b) where

$$\mathrm{Y^- + CH_3X \rightarrow YCH_3 + X^-} \tag{1b}$$

a correlation exists between the barrier in a certain direction (forward or reverse) and the looseness of the bond between the carbon and the leaving group.[4] How general is this relationship? Can it be shown to originate from principles which are not related to any particular modeling of the TS?

This paper applies a thermochemical approach[5] to deduce the relationship between barriers and TS structures for the archetype reaction class shown in:

$$\mathrm{Y + AX} \underset{\Delta E^{\ddagger}_{r}}{\overset{\Delta E^{\ddagger}_{f}}{\rightleftharpoons}} \mathrm{YA + X} \tag{2}$$

Thermochemical indexes are derived, which allow the calculation of the TS looseness from knowledge of the barriers $\Delta E^{\ddagger}_{f}$ and $\Delta E^{\ddagger}_{r}$ in the gas phase and, with appropriate modifications, also in solution phase. The significance of the looseness indexes and of the relationship between the barrier and TS structure is discussed and shown to stem from the nature of the activation process. Potential applications to other reaction classes are discussed.

Theoretical Analysis

A. Gas-Phase Identity Reactions. The transition state for the gas-phase reaction in eq 2 possesses one coordinate which corresponds to loosening of the A–X and Y–A bonds. The energy

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[1] Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642.

[2] Shaik, S. S. *Isr. J. Chem.* **1985**, *26*, 367.

[3] Shaik, S. S. *Can. J. Chem.* **1986**, *64*, 96.

[4] Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197 (pp 260–274).

[5] For previous mention of this approach see eq 42–44 in ref 4 (p 267), text footnote 1 in ref 3, and ref 2.

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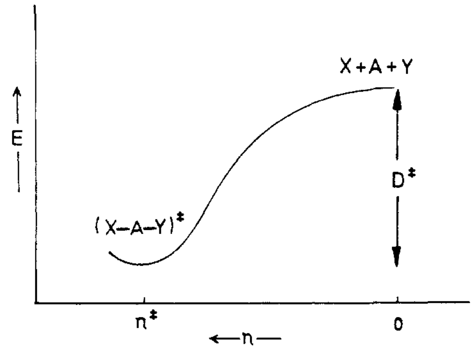


Figure 1. Dissociation curve of a three-center transition state. The horizontal coordinate describes bond-order changes (n) as a result of simultaneous stretching of the AX and AY bonds.

curve of this process, conducted to infinity, is shown in Figure 1. The fragments are the most stable gas-phase species A, Y, and X with appropriate charges for polar reactions.[5,6]

The binding energy of the TS, relative to the fragments, is $D^{\ddagger}$. If the decomposition curve in Figure 1 is smooth and involves no or only weak avoided crossings,[6] then the looseness of the TS can be defined absolutely, from the knowledge of $D^{\ddagger}$; the smaller the $D^{\ddagger}$ the closer the TS to its dissociation limit. This is, of course, the same idea that is inherent in the three-dimensional PES diagrams, used in physical organic chemistry to discuss TS structure.[7-10]

Consider first an identity reaction where X = Y. For this reaction class, the value of $D^{\ddagger}$ can be obtained from the thermochemical cycle in eq 3.[5] The cycle involves return of the TS

$$(\mathrm{XAX})^{\ddagger} \rightarrow \mathrm{X} + \mathrm{AX} \qquad \Delta E_1 = -\Delta E^{\ddagger} \tag{3a}$$

$$\mathrm{AX} \rightarrow \mathrm{A} + \mathrm{X} \qquad \Delta E_2 = D_{\mathrm{A-X}} \tag{3b}$$

$$(\mathrm{XAX})^{\ddagger} \rightarrow \mathrm{X} + \mathrm{A} + \mathrm{X} \qquad \Delta E = D^{\ddagger} \tag{3c}$$

to the ground state, followed by breaking of the A–X bond. The sum of the component processes is the fragmentation of the TS along the loosening coordinate of Figure 1. The binding energy $D^{\ddagger}$ reads then according to eq 4 which links the TS-binding to

$$D^{\ddagger} = D_{\mathrm{A-X}} - \Delta E^{\ddagger} \tag{4}$$

the barrier that is required to achieve this TS. This equation has been derived, by Leroy et al.[11] as well as by us.[5]

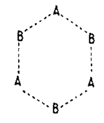
In an absolute sense, the tightness ($T^{\ddagger}$) of the TS bonds can be expressed by the ratio of the TS binding energy to the bond energy of the ground-state molecule. This is shown by eq 5a which, by substitution of eq 4, becomes eq 5b.

$$T^{\ddagger} = D^{\ddagger}/D_{\mathrm{A-X}} \tag{5a}$$

$$T^{\ddagger} = 1 - \Delta E^{\ddagger}/D_{\mathrm{A-X}} \qquad (L^{\ddagger} = 1 - T^{\ddagger}) \tag{5b}$$

Equation 5b defines a *thermochemical looseness* (*tightness*) *index* that varies between unity (for $\Delta E^{\ddagger} \approx 0$) and zero (for $\Delta E^{\ddagger} \approx D_{\mathrm{A-X}}$). Thus a barrier that approaches the bond energy limit is associated with an infinitely loose TS having $T^{\ddagger} = 0$, while a zero or a tiny barrier is associated with a tight TS having $T^{\ddagger} = 1$. A thermochemical link has thus been drawn between the experimental observable of the reaction, $\Delta E^{\ddagger}$, and the microscopic looseness of the TS. This microscopic looseness is associated with the *flatness* of the potential energy surface in the direction of the loosening mode.

The expression for $T^{\ddagger}$ applies, as is, to three-electron–three-center reactions such as atom transfer and group transfer reactions, as well as to four-electron–three-center reactions such as S_N2, proton transfer, and so on. The application to other identity reactions can be worked out using analogous thermochemical cycles to eq 3. For example, for six-electron–six-center reactions (3AB → 3AB),[12] with the hexagonal TS **1**, the binding energy



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is simply $D^{\ddagger} = 3D_{\mathrm{A-B}} - \Delta E^{\ddagger}$ and the $T^{\ddagger}$ index can be defined, in analogy with eq 5b, as follows:

$$T^{\ddagger} = \frac{D^{\ddagger}}{3D_{\mathrm{A-B}}} = 1 - \frac{\Delta E^{\ddagger}}{3D_{\mathrm{A-B}}} \tag{6}$$

The TS looseness for identity reactions is governed then, generally, by the reaction barrier and the ground-state bond energy; the greater the ratio, $\Delta E^{\ddagger}/D$, the looser the bonding in the TS. The principle underlying this conclusion is fundamental: that large barriers place the TS energetically close to its dissociation limit (eq 4 and 5b). Bonding looseness is then associated, in a thermochemical sense, with the largeness of the quantity $\Delta E^{\ddagger}/D$.

Before proceeding, a qualification is required regarding the application of the thermochemical indexes for geometric interpretation of experimental data. The $T^{\ddagger}$ indexes should not be used as universal measures of geometric parameters; comparisons should be limited to reaction series. To give an example for such a wrong application, consider eq 2 with A being CH_3 and H. When A is CH_3, both flattening of the methyl group and C–X lengthening contribute to the barrier and, hence, to the thermochemical looseness of the TS. In comparison, when A is H, only H–X lengthening contributes to the barrier and to the thermochemical looseness. Thus, an equal $T^{\ddagger}$ index for two, arbitrarily chosen, reactions will not translate generally to equal bond lengthening in the corresponding TSs. Thermochemically though, the sameness of $T^{\ddagger}$ means the same looseness as regards the flatness of the potential energy surface in the direction of the loosening mode (Figure 1).

B. Gas-Phase Nonidentity Reactions. Consider now the case of nonidentity reactions (X ≠ Y in eq 2). Two different thermochemical cycles can be used to derive the binding energy, $D^{\ddagger}$, of the TS (Figure 1). These cycles are detailed in eq 7 and 8 where

$$(\mathrm{YAX})^{\ddagger} \rightarrow \mathrm{Y} + \mathrm{AX} \qquad \Delta E_1 = -\Delta E^{\ddagger}_{\mathrm{f}} \tag{7a}$$

$$\mathrm{AX} \rightarrow \mathrm{A} + \mathrm{X} \qquad \Delta E_2 = D_{\mathrm{A-X}} \tag{7b}$$

$$(\mathrm{YAX})^{\ddagger} \rightarrow \mathrm{Y} + \mathrm{A} + \mathrm{X} \qquad \Delta E = D^{\ddagger} \tag{7c}$$

$$(\mathrm{YAX})^{\ddagger} \rightarrow \mathrm{YA} + \mathrm{X} \qquad \Delta E_1 = -\Delta E^{\ddagger}_{\mathrm{r}} \tag{8a}$$

$$\mathrm{YA} \rightarrow \mathrm{Y} + \mathrm{A} \qquad \Delta E_2 = D_{\mathrm{A-Y}} \tag{8b}$$

$$(\mathrm{YAX})^{\ddagger} \rightarrow \mathrm{Y} + \mathrm{A} + \mathrm{X} \qquad \Delta E = D'^{\ddagger} \tag{8c}$$

$\Delta E^{\ddagger}_{\mathrm{f}}$ and $\Delta E^{\ddagger}_{\mathrm{r}}$ are the barriers for the forward and reverse directions of reaction 2 (eq 2). If the reaction is a three-electron–three-center transformation (e.g., $\mathrm{Y}^{\bullet} + \mathrm{H{-}X} \rightarrow \mathrm{Y{-}H} + {}^{\bullet}\mathrm{X}$), then both cycles result in the same fragments, so that $D'^{\ddagger} = D^{\ddagger}$. Therefore, the TS binding energy reads:

$$D^{\ddagger} = D_{\mathrm{A-X}} - \Delta E^{\ddagger}_{\mathrm{f}} = D_{\mathrm{A-Y}} - \Delta E^{\ddagger}_{\mathrm{r}} \tag{9}$$

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(6) See discussion on pp 280–282 in ref 4.

(7) For a recent mathematical model, see: Harris, J. M.; Paul, J. L. *Isr. J. Chem.* **1985**, *26*, 325.

(8) W. P. Jenks, *Chem. Rev.* **1985**, *85*, 511 and references therein.

(9) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.

(10) More-O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274.

(11) The same equation has been derived for atom transfer reaction in: Leroy, G.; Sana, M. *THEOCHEM* **1986**, *136*, 283. Leroy, G.; Sana, M.; Tinant, A. *Can. J. Chem.* **1985**, *63*, 1447.

(12) For discussion of such six-center reactions, see: (a) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (b) Thompson, D. L.; Suzukawa, H. H., Jr. *Ibid.* **1977**, *99*, 3614. (c) Dixon, D. A.; Herschbach, D. R. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 162.

The average of the two expressions in eq 9 is also $D^\ddagger$, so that eq 9 becomes eq 10. Thus, the TS is seen to approach its dissociation limit (X + A + Y) the larger the sum of the barriers for the forward and reverse reactions.

$$D^\ddagger = \tfrac{1}{2}[(D_{\text{A-X}} + D_{\text{A-Y}}) - (\Delta E^\ddagger_{\text{f}} + \Delta E^\ddagger_{\text{r}})] \quad (10)$$

In conformity with foregoing arguments, an absolute measure of TS looseness can be expressed by the ratio of $D^\ddagger$ to the averaged sum of the bond energies for the ground-state molecules (A–X and A–Y). This is spelled out in eq 11a and 11b. Thus, as above,

$$T^\ddagger = \frac{D^\ddagger}{0.5(D_{\text{A-X}} + D_{\text{A-Y}})} \quad (11\text{a})$$

$$T^\ddagger = 1 - \frac{\Delta E^\ddagger_{\text{f}} + \Delta E^\ddagger_{\text{r}}}{D_{\text{A-X}} + D_{\text{A-Y}}} \quad (11\text{b})$$

$T^\ddagger$ is a thermochemical looseness index that varies between zero and unity (i.e., $T^\ddagger = 1$ for $\Sigma\Delta E^\ddagger = \Sigma D$).

For polar reactions (for example, four-electron–three-center transformations such as S_N2, proton transfer, and so on), the expressions for $D^\ddagger$ and $D'^\ddagger$ (in eq 7 and 8) are not identical. Thus, the cycle in eq 7 leads to the fragments Y:, A$^\bullet$, and X$^\bullet$, while the cycle of eq 8 to Y$^\bullet$, A$^\bullet$, and X:. A supplementary step must be added, then, to one of the cycles, to have both lead to the same and most stable fragments. The additional step for such reactions is eq 12 that must either be added to eq 7, if Y: is *less* stable than X:, or subtracted from eq 8, if Y: is *more* stable than X:. In either case the quantity that is added to $D^\ddagger$ or $D'^\ddagger$ is negative.

$$\text{Y:} + \text{X}^\bullet \rightarrow \text{Y}^\bullet + \text{X:} \qquad \Delta E = \text{IP}_{\text{Y:}} - \text{IP}_{\text{X:}} = \Delta\text{IP}_{\text{XY}} \quad (12)$$

Following the same procedure as above (eq 9 and 10), an expression for the TS binding energy can be derived for polar reactions, in eq 13. The corresponding tightness index follows and is given by eq 14. Thus, a TS of a polar reaction becomes looser as the sum of the forward and reverse barriers increases. An additional loosening effect now is the ionization potential imbalance (ΔIP) of the closed-shell groups, X: and Y:. The greater the IP imbalance, the looser the TS. In reality though, a large $\Sigma\Delta E^\ddagger$ is associated with a great IP imbalance so that qualitatively the ratio $\Sigma\Delta E^\ddagger/\Sigma D^\ddagger$ governs TS looseness.

$$D^\ddagger = \tfrac{1}{2}[(D_{\text{A-X}} + D_{\text{A-Y}}) - (\Delta E^\ddagger_{\text{f}} + \Delta E^\ddagger_{\text{r}}) - |\Delta\text{IP}_{\text{XY}}|] \quad (13)$$

$$T^\ddagger = 1 - \frac{\Delta E^\ddagger_{\text{f}} + \Delta E^\ddagger_{\text{r}} + |\Delta\text{IP}_{\text{XY}}|}{D_{\text{A-X}} + D_{\text{A-Y}}} \quad (14)$$

The fundamental principle of TS structure is projected once again, that large barriers are associated with thermochemically loose TSs which are close to their dissociation limits. Thereby, with the aid of eq 5b, 11b, and 14, the measured reaction kinetics can be instantly quantified and projected as TS looseness parameters which relate to the flatness of the potential energy surface.

C. Solvent Effect. The solvent may (or may not) affect the chemical identity of the dissociation limit fragments (in Figure 1). How would this affect the foregoing conclusions?

Consider, for example, the S_N2 reaction X:$^-$ + AX (A = alkyl). The gas-phase dissociation limit is X:$^-$ + A$^\bullet$ + X$^\bullet$ (symmetry adapted). In solution, depending on the solvent and the nature of A and X, the lowest energy *may* become triple ionic, X:$^-$ + A$^+$ + X:$^-$. Such a change, in the identity of the dissociation limit, is brought about by solvent-assisted avoided crossing.[6] Similarly, for three-electron–three-center reactions, the dissociation limit may be converted via solvent-assisted avoided crossing, from X$^\bullet$ + A$^\bullet$ + X$^\bullet$ to the (symmetry adapted) zwitterionic configuration X$^\bullet$ + A$^+$ + X:$^-$ (or X$^\bullet$ + A:$^-$ + X$^+$). Since the underlying principles of solvent assisted avoided crossing are common to all reaction classes, the main ideas are developed below by discussing S_N2 reactions.

In nonhydroxylic solvents and when A$^+$ is not highly stable (e.g., A = CH$_3$), the diradical (X:$^-$ + A$^\bullet$ + X$^\bullet$) and triple ionic (X:$^-$ + A$^+$ + X:$^-$) configurations are approximately of the same energy.[13a] Therefore, solvent-assisted avoided crossing will occur, when it does, at large A–X distances as shown in Figure 2a. In such cases, avoided crossing is not strong and the proper dissociation limit that governs TS loosenss is the diradical configuration.[6] Consequently, the former expressions for $T^\ddagger$ (e.g., eq 5b) are valid also in solution. Now, though, the $T^\ddagger$ indexes are calculated using the solution-phase barrier and, therefore, the looseness will refer to the molecular TS as well as to the deformations of the solvation shells surrounding it. These two effects can be separated as discussed elsewhere.[2]

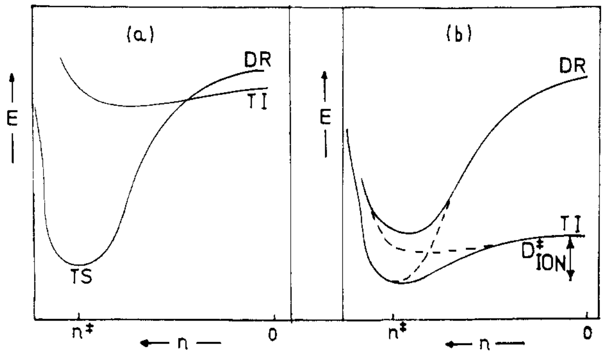

Figure 2. Dissociation curves of an S_N2 TS [(XAX)$^-$]‡ in solution. DR is the symmetry-adapted diradical configuration X:$^-$ + A$^\bullet$ + X$^\bullet$. TI is the triple ionic configuration X:$^-$ + A$^+$ + X:$^-$. The horizontal coordinate is the same as in Figure 1. (a) A case where DR and TI possess similar energies. Avoided crossing is weak and deleted. (b) A case of strong avoided crossing. Dashed lines show the intended correlation of the curves, while solid lines are curves after avoided crossing.

In hydroxylic solvents and when A$^+$ is stable (e.g., A = p-CH$_3$OC$_6$H$_4$CH$_2$, or A = H for proton-transfer reactions), the triple ion configuration crosses well below the diradical configuration, as shown in Figure 2b. In these cases the avoided crossing is significant and the TS possesses a significant triple ionic character.[13b] The triple ion configuration should be considered then as the proper dissociation limit of the TS, in harmony now with the description of the PESD model.[9,10] The corresponding binding energy of the TS will be modified, relative to the gas-phase reaction, and is designated as $D^\ddagger_{\text{ION}}$ in Figure 2b.

The expression for $D^\ddagger_{\text{ION}}$ derives from the cycle in eq 15 where

$$(\text{XAX})^\ddagger(\text{s}) \rightarrow \text{X(s)} + \text{AX(s)} \qquad \Delta E_1 = -\Delta E^\ddagger(\text{s}) \quad (15\text{a})$$

$$\text{AX(s)} \rightarrow \text{AX(g)} \qquad \Delta E_2 = -\Delta E_{\text{S}}(\text{AX}) \sim 0 \quad (15\text{b})$$

$$\text{AX(g)} \rightarrow \text{A}^\bullet(\text{g}) + \text{X}^\bullet(\text{g}) \qquad \Delta E_3 = D_{\text{A-X}} \quad (15\text{c})$$

$$\text{A}^\bullet(\text{g}) + \text{X}^\bullet(\text{g}) \rightarrow \text{A}^\bullet(\text{s}) + \text{X}^\bullet(\text{s}) \qquad \Delta E_4 = \Delta E_{\text{S}}(\text{A}^\bullet + \text{X}^\bullet) \sim 0 \quad (15\text{d})$$

$$\text{A}^\bullet(\text{s}) \rightarrow \text{A}^+(\text{s}) + \text{e}^- \qquad \Delta E_5 = \text{IP}[\text{A}^\bullet(\text{s})] \quad (15\text{e})$$

$$\text{X}^\bullet(\text{s}) + \text{e}^- \rightarrow \text{X:}^-(\text{s}) \qquad \Delta E_6 = -\text{EA}[\text{X}^\bullet(\text{s})] \quad (15\text{f})$$

$$(\text{XAX})^\ddagger(\text{s}) \rightarrow \text{X(s)} + \text{A}^+(\text{s}) + \text{X:}^-(\text{s}) \qquad \Delta E = D^\ddagger_{\text{ION}} \quad (15\text{g})$$

parenthetical (g) and (s) denote gas-phase and solution states, ΔE_{S} are solvation energies, while IP(s) and EA(s) are the adiabatic ionization potential and electron affinity in solution.[14] Note that the X(s) in eq 15a is written without specifying its number of electrons, which can be one or two. Thus, the cycle is applicable to four-electron–three-center reactions as well as, to three-electron–three-center reactions.

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[13] (a) See Table 12 (p 268) of ref 4. The diradical is more stable than the triple ion for some X's (e.g., I, Br, RS, ...) in hydroxylic solvents, and for most X's in nonhydroxylic solvents. (b) See discussion on pp 247 of ref 4.

[14] For evaluation of these quantities see: (a) Delahay, P. *Acc. Chem. Res.* **1982**, *15*, 40. (b) Ritchie, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 7313. (c) Shaik, S. S. *Ibid.* **1984**, *106*, 1227.

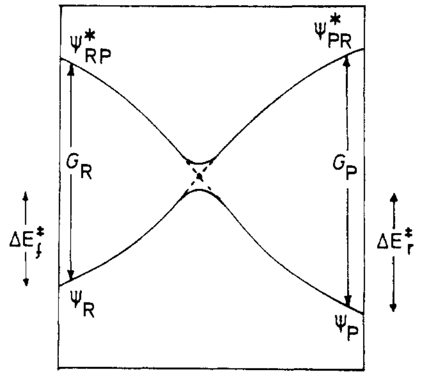

Figure 3. Avoided crossing diagram for a single step reaction R → P. Ψ_R and Ψ_P are the ground states of R and P while the Ψ^*'s are excited states (or configurations). G_R and G_P are energy gaps.

Summing up all the ΔE terms in eq 15 leads to $D^\ddagger_{ION}$ in eq 16. The corresponding tightness index, relative to the ground-state

$$D^\ddagger_{ION} = D_{A\text{-}X} + IP[A^\bullet(s)] - EA[X^\bullet(s)] - \Delta E^\ddagger(s) \quad (16)$$

molecule, A–X, becomes then eq 17, which generalizes all the cases

$$T^\ddagger = 1 - \frac{\Delta E^\ddagger(s) - (IP[A^\bullet(s)] - EA[X^\bullet(s)])}{D_{A\text{-}X}} \quad (17)$$

in the spectrum between Figures 2a and 2b, and should be used whenever in doubt about the magnitude of the avoided crossing. Equation 17 involves two loosening factors. The first one is $\Delta E^\ddagger(s)/D_{A\text{-}X}$, which would have been the only factor had we derived the expression for $D^\ddagger$ considering the *intended* correlation, in Figure 2b, to the diradical state. The second term in eq 17, $(IP - EA)/D_{A\text{-}X}$, reflects the stability of A^+ and X^-, relative to the radicals, and arises because we considered the correlation of the TS to the triple-ionic state, as is commonly done in the PESD models.[8,10] Thus, in any case, in the spectrum of Figure 2, part of the loosening movement is dominated by the diradical curve and part by the ionic curve.

The above two effects constitute together the *total thermochemical looseness* of the TS, but may signify the looseness in different senses. The first term, $(\Delta E^\ddagger/D)$, most likely takes into account geometric distortion effects of the TS relative to the ground-state molecule. The second term $((IP - EA)/D)$ may signify TS loosening in the sense of depletion of bonding electrons and localizing them on the ions. Some cases may exhibit an opposition of the two effects and result in TSs which are, at the same time, loose in the geometric sense but tight in the electron density sense. The X^- + $ArCH_2X$ system may be one such case where the opposition operates (p-NO_2 vs. p-CH_3O).[15]

Derivation of $T^\ddagger$ expressions for nonidentity reactions are analogous and follow the classification of Figure 2. Thus, in any case, there will exist a correlation between looseness and the ratio $\Sigma\Delta E^\ddagger/\Sigma D$, as in the gas-phase expressions (eq 11b and 14). Other basic properties, such as the stability of the ions, will also contribute to the looseness of the TS. Those additional effects may imply looseness in the sense of electron density depletion.

Discussion

The correlation between the looseness of the TS and the reaction barriers springs from a fundamental thermodynamic relation: that a high-energy TS, relative to its ground-state reactants and products, is close to the dissociation limit and, hence, possesses a loose structure in a thermochemical sense, i.e., a flat energy curve in the direction of the loosening mode.

In parallel, the same correlation can be derived from the SCD model,[1-4] to project a related fundamental nature of the activation process. In the SCD approach, the reaction profile, for a single-step reaction, arises from an avoided crossing as shown in Figure 3.[16] The TS will be established near the intersection point of the two curves which are initially separated by energy gaps, between the ground states and the excited states (configurations). To reach the crossing point, deformations are required which stabilize the excited states (configurations) and destabilize the ground states. These deformations occur to the extent sufficient for overcoming the gap and reaching the crossing point[1,16] (where TS is established by avoided crossing[17]). Thus, barriers derive from the deformations that are required to carry reactants and products to the locus of the TS. These deformations involve both molecular and solvational components.[2]

Table I. Barriers, TS Geometries, and Thermochemical Tightness Indexes for X^- + CH_3X → XCH_3 + X^- [a]

	X	$\Delta E^\ddagger$ (kcal/mol)	$(T^\ddagger)^b$	% $CX^\ddagger$
(1)	H	52.0	0.50	58.0
(2)	HCC	50.4	0.57	45.0
(3)	NC	43.8	0.62	44.8
(4)	CN	28.5	0.68	40.5
(5)	HO	21.2	0.77	30.4
(6)	HS	15.6	0.79	28.0
(7)	F	11.7	0.89	25.0
(8)	Cl	5.5	0.93	21.1

[a] Data from ref 1 and 18. [b] Calculated using eq 5b. $D_{C\text{-}X}$ values are tabulated in ref 1.

Looseness of the TS bonds and the barriers must then be related. The barrier in each direction ($\Delta E^\ddagger_f$, $\Delta E^\ddagger_r$) reflects the deformation of the corresponding reactant for this direction.[4] The sum of the barriers reflect, then, the total deformation of the reacting bonds and solvation shells of the TS, relative to the ground states (reactants and products). The greater the sum of the barriers, the more deformed the TS.

There is harmony then in the conclusion of the SCD model and the thermochemical approach. While the SCD model projects the root cause of the relationship between barriers and TS deformations, the thermochemical approach quantifies the relationship and provides thermochemical definitions of TS looseness, directly from the measured reaction kinetics.

The utility of the thermochemical index is projected in Table I which shows the ab initio data of Wolfe and collaborators,[18] for the gas-phase identity S_N2 reaction, which was analyzed previously using the SCD model.[1,2] Collected in the table are central barriers ($\Delta E^\ddagger$), thermochemical tightness indexes ($T^\ddagger$) calculated with eq 5b, and ab initio computed percentages of C–X bond cleavage in the TS (% $CX^\ddagger$). The thermochemical index, $T^\ddagger$, is seen to increase down the entries and to predict, therefore, that TS looseness should *decrease* toward entry 8. This trend is seen to be dominated by the barrier such that the higher the barrier the smaller the $T^\ddagger$ and, accordingly, the looser should the TS be. These thermochemical predictions are in harmony with the geometric index, % $CX^\ddagger$, which shows that the TS, whose calculated $T^\ddagger$ is the smallest, indeed suffers the largest percentage of bond cleavage. The linear correlation between % $CX^\ddagger$ and $T^\ddagger$ is good (cc = 0.978), so that given a barrier, the corresponding TS geometry can instantly be predicted. The relationship between barrier height and TS looseness seems to be quite general and a few such examples follow. Thus, a variety of isotope effect measurements show that the catalyses of an S_N2 reaction are accompanied by tightening of the TS.[19] Computational results of extended series of S_N2 reactions show a correlation between

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[15] See pp 279 and 237 in ref 4, as well as isotope effect data in: Hayami, J.; Hihara, N.; Tanaka, N.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 831.

[16] See p 201 of ref 4 and, Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692.

[17] For discussions of avoided crossing mechanisms in chemistry see: Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982. Salem, L.; Leforestier, C.; Segal, G.; Whetemore, R. *J. Am. Chem. Soc.* **1975**, *97*, 479.

[18] Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694.

[19] (a) Gray, C. H.; Coward, J. K.; Schowen, K. B.; Schowen, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 4351. (b) Wong, O. S.-L.; Schowen, R. L. *Ibid.* **1983**, *105*, 1951. (c) Rodgers, J.; Femec, D. A.; Schowen, R. L. *Ibid.* **1982**, *104*, 3263. (d) Hegazi, M. F.; Borchardt, R. T.; Schowen, R. L. *Ibid.* **1979**, *101*, 4359. (e) Mihel, I.; Knipe, J. O.; Coward, J. K.; Schowen, R. L. *Ibid.* **1979**, *101*, 4349.

the looseness of the TS with the sum of forward and reverse barriers[20,21] as well as with the intrinsic barrier.[22] In nucleophilic vinylic attacks, a correlation has been noted between barriers and the extent of structural deformations experienced by the reactants.[23] Similar observations have been made for radical addition reactions to olefins.[24,25] Other transformations, such as three-electron–three-center exchange reactions ($X^{\bullet} + X_2 \rightarrow X_2 + X^{\bullet}$),[26] and six-electron–six-center exchange reactions,[12] exhibit the same general trend; that TSs become looser as barriers increase. All these observations reflect the two fundamental conclusions discussed in this work: (a) that high barriers are associated with TSs which are close to their dissociation limits, and (b) that reaction barriers derive from the deformations that are required to carry the ground-state molecules to the TS and that in all the above examples, the principal deformation which establish TSs are apparently bond stretchings. These two fundamental features of reactivity provide the link between the kinetic observable of a reaction and the structure of its TS.

Conclusions

The looseness of a TS can be defined, thermochemically, directly from the measured reaction kinetics. Thus, loose bonding is assigned to a TS which approaches its dissociation limit and possesses thereby a small binding energy, $D^{\ddagger}$ (Figure 1). Large reaction barriers ($\Delta E^{\ddagger}_{f}$ and $\Delta E^{\ddagger}_{r}$) weaken the binding energy and hence loosen the reacting bonds of the TS. This correlation can be quantified as $T^{\ddagger}$ indexes that define the *thermochemical tightness* of the TS, relative to its ground-state molecules, on a scale from zero to unity (eq 5b, 6, 11b, 14, and 17). Derivations of $T^{\ddagger}$ indexes for different classes of reactions[27] reveal a common feature, that higher reaction barriers ($\Sigma\Delta E^{\ddagger}$) are associated with thermochemically loose TSs. A small $T^{\ddagger}$ index is associated with a flat surface in the direction of the loosening mode. A correlation, between the geometric looseness of the TS and the $T^{\ddagger}$ index, is expected whenever bond stretchings are the principal deformations which are required to achieve the TS.

For the identity S_N2 reaction, a one-to-one correlation is obtained between the thermochemical index, $T^{\ddagger}$, and the geometric index, % $CX^{\ddagger}$ (percentage of bond cleavage; see Table I). Further exploration is required to specify reaction classes in which the thermochemical and geometric looseness of the TS conveys the same sense. In such a reaction series, a direct mapping may be possible of transition-state structures from the kinetic measurements.

Yet, thermochemical looseness may not always convey the same sense as geometric looseness. Thus, for example, mere flattening of the CH_3 group in CH_3X weakens the C–X bond so it approaches its dissociation limit. In a thermochemical sense, this is equivalent to loosening of this bond, even if no change in its length has occurred. Other types of thermochemical looseness that do not require geometric loosening are depletion of bonding electrons due to bond ionicity in the TS (section I.C.) and antibonding interaction between electron pairs which contribute to high barriers. Included also are solvent reorganization effects[2] whose contribution to barriers do not reflect loosening of the molecular transition state but rather "loosening" of the solvation shells about the reactants.[28]

The discrepancy between $T^{\ddagger}$ index of a TS and its geometric looseness is important then, for it may inform something specific about the activation process; for example, the type of deformations which do not involve stretching of the reacting bonds, but which nonetheless are required in order to achieve TS. Vital research may become then to ascertain what senses of looseness are detected by current experimental methodology of physical organic chemistry (e.g., isotope effect, etc.), and what kind of approaches should be devised to probe, for example, electron density vs. geometric looseness effects.

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(20) Shaik, S. S.; Schlegel, H. B.; Wolfe, S., manuscript in preparation.

(21) Harris, J. M., private communication. Isotope effect measurements on the Menschutkin reaction indicate tighter transition states for smaller $\Sigma\Delta E^{\ddagger}$.

(22) Shaik, S. S. Presented in the "Nucleophilicity Symposium" at the 190th National Meeting of the American Chemical Society, Chicago, 1985. This correlation holds because $2\Delta E_{o}^{\ddagger} = \Delta E_{f}^{\ddagger} + \Delta E_{r}^{\ddagger}$ if the quadratic term is neglected in the Marcus equation ($\Delta E^{\ddagger}_{o}$ – intrinsic barrier).

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(26) Koshi, M.; Ito, H.; Matsui, H. *Chem. Phys. Lett.* **1983**, *103*, 180. Note that Leroy et al. (ref 11) found that barriers for the reactions $\dot{Y} + HX$ can be reproduced with the assumption of a constant TS geometry (25% bond elongation). In accord, the $T^{\ddagger}$ indexes, calculated using these barriers, are approximately constant, $T^{\ddagger} = 0.867 \pm 0.034$.

(27) Expressions for elimination reactions, NVS, heterolytic cleavage, and radical additions to olefins are available. All the expressions include $\Sigma\Delta E^{\ddagger}$ as a loosening factor.

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