

The reaction force and the transition region of a reaction

Alejandro Toro-Labbé · Soledad Gutiérrez-Oliva ·
Jane S. Murray · Peter Politzer

Received: 30 September 2008 / Accepted: 20 November 2008 / Published online: 16 December 2008
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Abstract The reaction force $\mathbf{F}(\mathbf{R})$ and the position-dependent reaction force constant $\kappa\mathbf{F}(\mathbf{R})$ are defined by $\mathbf{F}(\mathbf{R}) = -\partial V(\mathbf{R})/\partial \mathbf{R}$ and $\kappa(\mathbf{R}) = \partial^2 V(\mathbf{R})/\partial \mathbf{R}^2$, where $V(\mathbf{R})$ is the potential energy of a reacting system along a coordinate \mathbf{R} . The minima and maxima of $\mathbf{F}(\mathbf{R})$ provide a natural division of the process into several regions. Those in which $\mathbf{F}(\mathbf{R})$ is increasing are where the most dramatic changes in electronic properties take place, and where the system goes from activated reactants (at the force minimum) to activated products (at the force maximum). $\kappa(\mathbf{R})$ is negative throughout such a region. We summarize evidence supporting the idea that a reaction should be viewed as going through a transition *region* rather than through a single point transition state. A similar conclusion has come out of transition state spectroscopy. We describe this region as a chemically-active, or electronically-intensive, stage of the reaction, while the ones that precede and follow it are structurally-intensive. Finally, we briefly address the time dependence of the reaction force and the reaction force constant.

Keywords Reaction force · Reaction force constant · Time-dependence · Transition region · Transition state spectroscopy

A. Toro-Labbé (✉) · S. Gutiérrez-Oliva
Laboratorio de Química Teórica Computacional (QTC),
Facultad de Química, Pontificia Universidad Católica de Chile,
Vicuña Mackenna 4860, Casilla 306, Correo 22,
Santiago, Chile
e-mail: atola@puc.cl

J. S. Murray · P. Politzer
Department of Chemistry, University of New Orleans,
New Orleans, LA 70148, USA

J. S. Murray · P. Politzer
Department of Chemistry, Cleveland State University,
Cleveland, OH 44115, USA

The reaction force

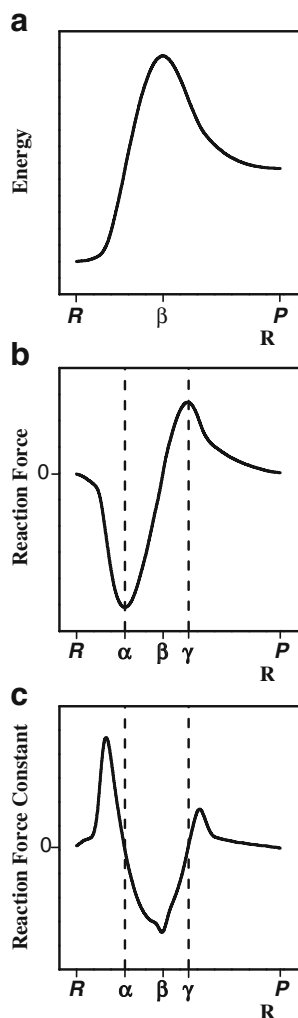
Some years ago was introduced the concept of the reaction force $\mathbf{F}(\mathbf{R})$ [1], based upon the classical expression for a force as the negative gradient of a potential energy. For a chemical or physical process,

$$\mathbf{F}(\mathbf{R}) = -\frac{\partial V(\mathbf{R})}{\partial \mathbf{R}} \quad (1)$$

in which $V(\mathbf{R})$ is the profile of the potential energy of the total system along some well-defined path \mathbf{R} from reactants to products; this is in general the intrinsic reaction coordinate [2, 3]. For a one-step process proceeding through an activation barrier, $V(\mathbf{R})$ has a form such as is shown in Fig. 1(a); the corresponding $\mathbf{F}(\mathbf{R})$ is in Fig. 1(b). Note that \mathbf{R} is being treated as a vector, always in the direction from the reactants to the products; for the reverse process, \mathbf{R} would increase in the opposite direction and $\mathbf{F}(\mathbf{R})$ would be the negative (i.e., mirror image) of that in Fig. 1(b).

It follows from Eq. (1) that $\mathbf{F}(\mathbf{R})$ has a minimum and a maximum at the inflection points of $V(\mathbf{R})$, at $\mathbf{R}=\alpha$ and $\mathbf{R}=\gamma$. Fig. 1 (b) shows that these divide the reaction into three regions: reactants (\mathbf{R}) $\rightarrow \alpha$, $\alpha \rightarrow \gamma$ and $\gamma \rightarrow$ products (\mathbf{P}). We have analyzed a number of processes in terms of the reaction force and these three regions, including intra- and intermolecular proton transfers and other molecular rearrangements [4–9], conformational changes [6, 10], bond dissociation/formation [11–13], S_N2 substitution [14, 15] and addition to a double bond [16]. (For reactions having more than one potential energy barrier, $\mathbf{F}(\mathbf{R})$ has several minima and maxima, and there are accordingly more than three regions [9].) For reviews, see Politzer et al. [17] and Toro-Labbé et al. [18, 19]. These studies have shown that, in general, each of the regions defined by $\mathbf{F}(\mathbf{R})$ is characterized by a certain type of change in the progression from reactants to products.

Fig. 1 Profiles of energy (a), reaction force (b) and reaction force constant (c) for a generic elementary step



In the first region, prior to the minimum of $F(\mathbf{R})$, what occurs are primarily structural distortions of the reactants - bond stretching, angle bending, etc. The resistance to these changes, which are a preparation for subsequent steps, gives rise to an increasingly negative (retarding) reaction force, which reaches its greatest strength at $R=\alpha$, the minimum of $F(\mathbf{R})$. At this point, the system can be said to consist of distorted (or activated) states of the reactants.

The second region, from the $F(\mathbf{R})$ minimum at α to its maximum at γ , is where the major portion of the transition from reactants to products takes place. There are typically rapid and extensive changes in electronic properties, such as electrostatic potentials and ionization energies. New bonds may begin to form. All of this produces a growing positive driving force, starting at $R=\alpha$, that gradually overcomes the retarding one. At $R=\beta$, they are equal in magnitude and exactly balance, after which the driving force is dominant and continues to increase until it achieves its maximum at $R=\gamma$.

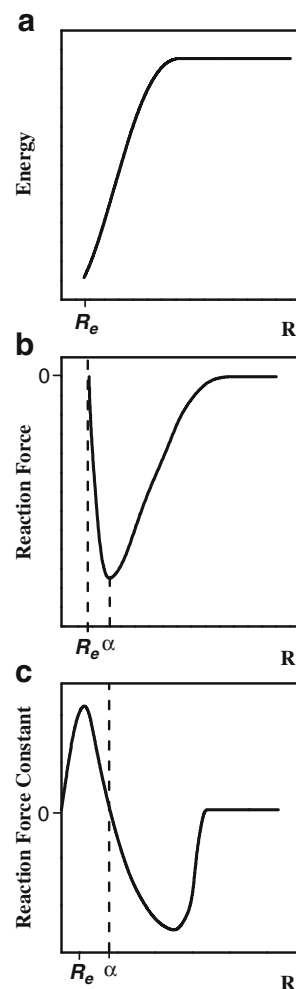
At $R=\gamma$, the system has reached what can be described as distorted (or activated) states of the products. The last

region, after γ , involves primarily structural relaxation of the system to its final state, $F(\mathbf{R})$ decreasing to zero for the products at equilibrium.

The general pattern, then, is that while structural changes occur throughout a process, they are the dominant factors in the first and the third regions. Variations in electronic properties, on the other hand, tend to be slow and gradual in these regions, and much more rapid and extensive in the intervening transition-to-products region. It should be noted that the three regions that have been discussed are not defined arbitrarily, but rather by the extrema of $F(\mathbf{R})$, and hence - by Eq. (1) - are a rigorous consequence of the particular form of $V(\mathbf{R})$.

For barrierless bond dissociation/formation, $V(\mathbf{R})$ is as depicted in Fig. 2(a), and the resulting $F(\mathbf{R})$ is in Fig. 2(b). The magnitude of R is the length of the bond being broken or formed, and its direction is toward the separate fragments in dissociation (Fig. 2) and toward the equilibrium bond length R_e in formation. Since $V(\mathbf{R})$ now has only one inflection point, $F(\mathbf{R})$ has just one extremum, a minimum for dissociation and a maximum for formation. The extremum defines two regions, with characteristics analo-

Fig. 2 Profiles of energy (a), reaction force (b) and reaction force constant (c) for a generic barrierless bond dissociation/formation process



gous to those described above. Thus the region between R_c and α corresponds (in dissociation) to increasing stretching of the bond, opposed by a growing retarding force, while the region after α can be viewed as transition to products (fragments). Reaction force analysis of bond dissociation/formation reveals some remarkable features, which are discussed in detail elsewhere [11–13].

An important aspect of reaction force analysis is its natural decomposition of an activation energy into two components:

$$\begin{aligned}\Delta E_{\text{act}} &= V(\beta) - V(\text{reactants}) \\ &= [V(\beta) - V(\alpha)] + [V(\alpha) - V(\text{reactants})] \quad (2) \\ &= \Delta E_{\text{act},2} + \Delta E_{\text{act},1}\end{aligned}$$

$\Delta E_{\text{act},1}$ is the energy requirement for the first region, reactants $\rightarrow \alpha$, which is needed to overcome the resistance of the system to the primarily structural changes that are taking place. $\Delta E_{\text{act},2}$ is the energy required for the first part of the transition to products, $\alpha \rightarrow \beta$.

Examining these two contributions to ΔE_{act} can provide considerable insight into the activation process [15–19]. It can also help to elucidate the role of an external agent, e.g., a solvent or a catalyst. In two of the three examples that we have so far investigated (two involving solvents and one a catalyst), we have found that they affect $\Delta E_{\text{act},1}$ much more than $\Delta E_{\text{act},2}$ [15, 16, 18].

The reaction force constant

A logical extension of the concept of the reaction force is the position-dependent reaction force constant $\kappa(\mathbf{R})$, the second derivative of $V(\mathbf{R})$:

$$\kappa(\mathbf{R}) = \frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}^2} = -\frac{\partial \mathbf{F}(\mathbf{R})}{\partial \mathbf{R}} \quad (3)$$

$\kappa(\mathbf{R})$ has been discussed by Jaque et al. [20] and subsequently by Murray et al. [12, 13].

The variation of $\kappa(\mathbf{R})$ with \mathbf{R} for the two types of $V(\mathbf{R})$ that have been mentioned can be seen in Figs. 1(c) and 2(c). $\kappa(\mathbf{R})$ is positive in the structurally-dominated regions, with maxima at the inflection points of $\mathbf{F}(\mathbf{R})$. It then passes through zero at the extrema of $\mathbf{F}(\mathbf{R})$, and is negative during the transition-to-products, with a minimum at β , the inflection point of $\mathbf{F}(\mathbf{R})$. The fact that $\kappa(\mathbf{R})$ is negative throughout the region from α to γ is of considerable significance, as shall now be discussed.

In a process such as that represented by Fig. 1(a), it is customary to focus upon the maximum of $V(\mathbf{R})$, at $R=\beta$, as the transition *state* in the progression from reactants to products. It is characterized, indeed identified, by there being a single negative force constant, for one degree of freedom (along R). However the reaction force constant

$\kappa(\mathbf{R})$ is negative not only at the single point $R=\beta$, but in the entire region between the $\mathbf{F}(\mathbf{R})$ minimum at α and its maximum at γ . This strongly supports the idea of a transition *region* (rather than single state), which came out of our observation that the most dramatic changes in computed electronic properties occur between α and γ , as mentioned earlier.

There is also more direct evidence. For the proton transfer,



Jaque et al. calculated the force constant $k(\mathbf{R})$ for movement along the reaction coordinate [20]; this invokes the projection methodology of Miller et al. [21]. $k(\mathbf{R})$ was found to be negative between the minimum and the maximum of $\mathbf{F}(\mathbf{R})$ for the reaction in eq. (4)! A similar result has been obtained for the addition of HCl to $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$ [16].

Additional support comes from analyses of the dissociations of diatomic molecules. Force constants $k(\mathbf{R})$ corresponding to bond-stretching were obtained from the very accurate experimentally-based extended Rydberg $V(\mathbf{R})$ [12], and also from Hartree-Fock and density functional computations [13]. By all of these procedures, the bond-stretching force constants became negative in the immediate vicinities of the respective $\mathbf{F}(\mathbf{R})$ minima, and remained so as the atom separation continued to increase.

Thus, as has been pointed out earlier [13, 18–20], reaction force and reaction force constant analyses indicate that it is more realistic to think of a process as going through a transition *region* rather than focusing upon a single point transition *state*. We wish now to draw attention to the fact that similar conclusions have been reached by a different route.

Transition state spectroscopy

During the past several decades, there has been considerable interest and activity, both computational and experimental, in characterizing the transient intermediate configurations through which a reacting system passes in going from reactants to products [22–30]. It has been found possible to observe these species spectroscopically (transition state spectroscopy, TSS), using very short laser pulses, on a femtosecond time scale (10^{-15} s) [25–30].

In the context of the discussion in the previous section, what we wish to point out is how “transition state” is defined in TSS. It encompasses all of the states of the system along the reaction path, from perturbed forms of the reactants to perturbed forms of the products [27, 29, 30]; it “embraces the entire process of bond breaking and bond making, ...[29]. This certainly sounds very much like the transition-to-products region that is identified by the reaction

force and the reaction force constant, which also establish its boundaries, as the minimum and maximum of $\mathbf{F}(\mathbf{R})$.

Transition state spectroscopy offers insight into temporal aspects of reactions [23, 27, 28]. The time dependence of the reaction force and the reaction force constant have not previously been addressed, although both can be viewed as functions of time as well as position along R. To express $F(t)$ and $\kappa(t)$, at least formally, we follow Zewail et al. [27, 30], and make use of Eq. (1),

$$\frac{\partial V}{\partial t} = \frac{\partial V}{\partial \mathbf{R}} \cdot \frac{\partial \mathbf{R}}{\partial t} = -\mathbf{F} \cdot \frac{\partial \mathbf{R}}{\partial t} \quad (5)$$

or

$$\mathbf{F}(t) = -\frac{\partial V/\partial t}{\partial \mathbf{R}/\partial t} = -\frac{1}{\mathbf{v}} \cdot \frac{\partial V}{\partial t} \quad (6)$$

in which \mathbf{v} is the velocity along R. Furthermore,

$$\frac{\partial \mathbf{F}}{\partial t} = \frac{\partial \mathbf{F}}{\partial \mathbf{R}} \cdot \frac{\partial \mathbf{R}}{\partial t} \quad (7)$$

Introducing Eq. (3) and rearranging gives,

$$\kappa(t) = -\frac{\partial \mathbf{F}/\partial t}{\partial \mathbf{R}/\partial t} = -\frac{1}{\mathbf{v}} \cdot \frac{\partial \mathbf{F}}{\partial t}. \quad (8)$$

Thus, through Eqs. (6) and (8), we have both the reaction force and the reaction force constant as functions of time, in terms of quantities that can in principle be determined via transition state spectroscopy [23, 27, 28].

Discussion and summary

The maximum of $V(\mathbf{R})$ is an important point along a reaction coordinate. It determines the activation energy, it is where the retarding and the driving components of $\mathbf{F}(\mathbf{R})$ exactly balance, and it corresponds to the most negative value of $\kappa(\mathbf{R})$. However this is not the only point along R at which $\kappa(\mathbf{R})$ is negative; it is negative for all of the configurations of the system between the minimum and the maximum of $\mathbf{F}(\mathbf{R})$, i.e., between the activated reactants and the activated products. These negative $\kappa(\mathbf{R})$, together with the computationally observed patterns of changes in electronic properties, indicate that this entire region should be viewed as a sequence of transient, unstable configurations or transition states, a *transition region* or *space* - exactly the concept that comes out of transition state spectroscopy! In general terms, this region may be described as a chemically-active, or electronically-intensive, stage of the reaction, in contrast to the structurally-intensive stages that precede and follow it.

Acknowledgements The authors wish to thank financial support from FONDECYT through projects 1060590, 11070197 and 7080164 and FONDAP, project 11980002 (CIMAT).

References

1. Toro-Labbé A (1999) J Phys Chem A 103:4398–4403. doi:10.1021/jp984187g
2. Fukui K (1981) Acc Chem Res 14:363–368. doi:10.1021/ar00072a001
3. Gonzalez C, Schlegel HB (1990) J Phys Chem 94:5523–5527. doi:10.1021/j100377a021
4. Jaque P, Toro-Labbé A (2000) J Phys Chem A 104:995–1003. doi:10.1021/jp993016o
5. Toro-Labbé A, Gutiérrez-Oliva S, Concha MC, Murray JS, Politzer P (2004) J Chem Phys 121:4570–4576. doi:10.1063/1.1777216
6. Martínez J, Toro-Labbé A (2004) Chem Phys Lett 392:132–139. doi:10.1016/j.cplett.2004.05.034
7. Gutiérrez-Oliva S, Herrera B, Toro-Labbé A, Chermette H (2005) J Phys Chem A 109:1748–1751. doi:10.1021/jp0452756
8. Rincón E, Jaque P, Toro-Labbé A (2006) J Phys Chem A 110:9478–9485. doi:10.1021/jp062870u
9. Herrera B, Toro-Labbé A (2007) J Phys Chem A 111:5921–5926. doi:10.1021/jp065951z
10. Bulat FA, Toro-Labbé A (2002) Chem Phys Lett 354:508–517. doi:10.1016/S0009-2614(02)00186-0
11. Politzer P, Murray JS, Lane P, Toro-Labbé A (2007) Int J Quantum Chem 107:2153–2157. doi:10.1002/qua.21400
12. Politzer P, Murray JS (2008) Collect Czech Chem Commun (in press)
13. Murray JS, Toro-Labbé A, Clark T, Politzer P (2009) J Mol Model (in press)
14. Politzer P, Burda JV, Concha MC, Lane P, Murray JS (2006) J Phys Chem A 110:756–761. doi:10.1021/jp0582080
15. Burda JV, Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P (2007) J Phys Chem A 111:2455–2458. doi:10.1021/jp0709353
16. Burda JV, Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P, to be submitted
17. Politzer P, Toro-Labbé A, Gutiérrez-Oliva S, Herrera B, Jaque P, Concha MC, Murray JS (2005) J Chem Sci 117:467–472. doi:10.1007/BF02708350
18. Toro-Labbé A, Gutiérrez-Oliva S, Murray JS, Politzer P (2007) Mol Phys 105:2619–2625. doi:10.1080/00268970701604663
19. Toro-Labbé A, Gutiérrez-Oliva S, Politzer P, Murray JS in Theory of Chemical Reactivity, P. Chattaraj (Ed), Taylor-Francis, Boca Raton, FL, in press
20. Jaque P, Toro-Labbé A, Politzer P, Geerlings P (2008) Chem Phys Lett 456:135–140. doi:10.1016/j.cplett.2008.03.054
21. Miller WH, Handy NC, Adams JE (1980) J Chem Phys 72:99–112. doi:10.1063/1.438959
22. Foth H-J, Polanyi JC, Telle HH (1982) J Phys Chem 86:5027–5041. doi:10.1021/j100223a001
23. Mayne HR, Polanyi JC, Sathyamurthy N, Raynor S (1984) J Phys Chem 88:4064–4068. doi:10.1021/j150662a042
24. Engel V, Bacic Z, Schinke R, Shapiro M (1985) J Chem Phys 82:4844–4849. doi:10.1063/1.448653
25. Smith IWM (1987) Nature 328:760–761. doi:10.1038/328760a0
26. Collings BA, Polanyi JC, Smith MA, Stollow A, Tarr AW (1987) Phys Rev Lett 59:2551–2554. doi:10.1103/PhysRevLett.59.2551
27. Rosker MJ, Dantus M, Zewail AH (1988) J Chem Phys 89:6113–6127. doi:10.1063/1.455427
28. Dantus M, Rosker MJ, Zewail AH (1988) J Chem Phys 89:6128–6140. doi:10.1063/1.455428
29. Polanyi JC, Zewail AH (1995) Acc Chem Res 28:119–132. doi:10.1021/ar00051a005
30. Zewail AH (2000) J Phys Chem A 104:5660–5694. doi:10.1021/jp001460h